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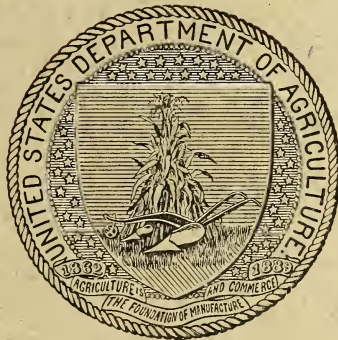
U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS—BULLETIN No. 33.
MILTON WHITNEY, Chief.

CALCIUM SULPHATE IN AQUEOUS SOLUTIONS:

A CONTRIBUTION TO THE STUDY OF
ALKALI DEPOSITS.

BY

FRANK K. CAMERON AND JAMES M. BELL.



WASHINGTON:
GOVERNMENT PRINTING OFFICE.
1906.

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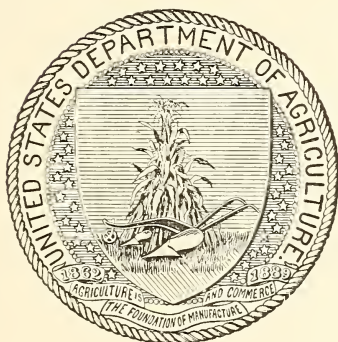
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LETTER OF TRANSMITTAL.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF SOILS,

Washington, D. C., April 4, 1906.

SIR: I respectfully transmit herewith the manuscript of a technical paper entitled "Calcium Sulphate in Aqueous Solutions: a Contribution to the Study of Alkali Deposits," which I recommend to be published as Bulletin No. 33 of the Bureau of Soils.

Respectfully,

MILTON WHITNEY,
Chief of Bureau.

HON. JAMES WILSON,
Secretary of Agriculture.

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CALCIUM SULPHATE IN AQUEOUS SOLUTIONS.

INTRODUCTION.

Calcium sulphate in its various modifications is of considerable importance in agricultural investigations. It is probably a common constituent of soils, although in the surface soils of humid regions it is seldom present in noticeable amounts. In arid regions, however, it is a common mineral component of the soil, sometimes forming a large percentage of the whole, even in soils of considerable agricultural importance. For instance, in the Pecos Valley, New Mexico, there occurs an important soil type, the Gypsum loam or "yeso," which is almost entirely gypsum, the dihydrate of calcium sulphate,^a with possibly some anhydrite—the salt free from combined water.

Calcium sulphate exists in several forms. The most common is known as gypsum, which is the dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and is found widely distributed in nature both in massive deposits and in well-defined crystals or crystal masses. A hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) also exists and is the common form in which calcium sulphate separates from solutions in boiler and pan scales. It is a metastable form; that is, it is stable under a wide range of conditions, but only in the absence of a more stable form. Under ordinary conditions it would change more or less gradually to gypsum or anhydrite, if some of the latter were brought into contact with it. Natural anhydrite (CaSO_4) or calcium sulphate containing no water of crystallization, is found in nature generally in deep-seated regions where it has separated from saline solutions in past times and been subsequently protected from the continued action of moist air. It should be observed, however, that the anhydrite must have separated from solutions of rather high concentration with respect to the more soluble salts, for gypsum is the form which separates from such a solution when the concentration of the other salts is low. Where anhydrite has been found at or near the surface and in such position that it comes in contact with moisture, it is always associated with gypsum, into which it is slowly and gradually changing. Another form of anhydrite, the so-called artificial anhy-

^a Report No. 64, Field Operations of the Division of Soils, U. S. Dept. Agr. (1899), p. 67.

drite, can be prepared in the laboratory under certain well-defined conditions, and differs from the natural anhydrite mainly in having a greater solubility and possessing only metastability. Several other forms of calcium sulphate have been described from time to time, but their existence has not been confirmed by subsequent investigation.

These several forms of calcium sulphate are each stable under certain well-defined conditions, but, with disturbance or changes in the conditions, there may be a more or less ready transformation of one form into another. Thus under ordinary conditions of temperature, and in contact with the air, gypsum is the stable form. But both the hemihydrate and anhydrite can and often do exist under these conditions as metastable forms, because the transformation to the more stable gypsum is very slow. In contact with pure water, gypsum is the stable form up to a temperature of about 66° C., when natural anhydrite becomes the stable form, but the solubility of gypsum has frequently been determined at temperatures up to 100° C., because at these higher temperatures the transformation of the less stable gypsum to the more stable anhydrite is quite slow. The temperature at which gypsum ceases to be stable and anhydrite becomes the stable form is lowered by the presence of other salts, being about 33° in a saturated solution of sodium chloride and about 11° in a saturated solution of magnesium chloride. Nevertheless, the solubility of gypsum can be determined in this latter solution, since gypsum can be kept in contact with it for weeks at ordinary temperatures without appreciable change into the more stable form of anhydrite.

The slowness with which these transformations take place long proved a serious stumbling block in studies of calcium sulphate solutions and led to many misconceptions regarding its properties and conduct toward other substances. But recent investigations, notably the brilliant series carried out by van 't Hoff with Meyerhoffer and other coworkers, have yielded an extensive and precise knowledge of the transformations of the several forms of calcium sulphate and the conditions under which the several forms exist in stable equilibrium.

The solubility of calcium sulphate in pure water is considerable, a saturated solution at ordinary temperatures containing upward of 0.2 per cent of the salt. Moreover, with this substance, there is a marked tendency to the formation of supersaturated solutions, and solutions have been observed containing several times the amount of calcium sulphate that can be dissolved under equilibrium conditions. For this reason, the large number of determinations of the solubility of calcium sulphate which have been made in the past are very discordant, and this fact probably accounts also for some of the many other difficulties which have arisen in the study of this substance both in the laboratory and in the field. Recent careful work, however, by several investigators has established the real solubility of this substance with a very

satisfactory degree of exactness. With rise of temperature the solubility of calcium sulphate gradually increases to a maximum which is reached at about 40°C ., the solution then containing about 0.21 per cent. With further increase in temperature the solubility steadily decreases, and at 100°C . it is less soluble than in ice water. The solubility may be increased over three times by the addition of sodium chloride and over four times by magnesium chloride, a reaction taking place, to some extent at least, between the calcium sulphate and the other salt whereby calcium chloride is formed, and at the same time a sulphate of sodium or magnesium, as the case may be. Undoubtedly it is in this manner that the soluble sulphates are formed in many of the cases of "alkali" found in arid areas, where sodium chloride is the predominating salt in contact with soils containing much calcium sulphate. A similar reaction takes place between sodium chloride and calcium carbonate, and a chemical classification of alkali conditions can be made very conveniently on this basis, as was proposed in Bulletin No. 17 of this Bureau, and it is from this point of view that this bulletin has been prepared, our present knowledge of the action of water and other salts on calcium sulphate being brought into an orderly arrangement as a chapter in the larger study of the chemistry of "alkali." A somewhat similar investigation on the effect of water, salts, and carbon dioxide upon calcium carbonate is in progress, together with a study of absorption and leaching phenomena, which it is believed will give a clear and comprehensive view of the chemical and physical principles involved in the management of soils containing alkali, and which is already suggesting important modifications of the treatment of this difficult and vexatious problem in the agriculture of irrigated areas. Intimately connected with this problem is the use of irrigation waters carrying sulphates and calcium salts, as well as the use of waters carrying other salts upon lands containing gypsum, and the effects which may reasonably be anticipated.

It has popularly been supposed that the composition of a drainage water from an alkaline soil could be easily predicated from a knowledge of the respective solubilities of the salts composing the alkali, and even the recent literature contains discussions of this subject based on the erroneous notion that the several components of a mixture will necessarily be removed in the order of the individual solubilities. That such is not the case, but that the relation of the vapor pressures of the solution and of the solid components, the formation of new molecular species (such as so-called double salts), as well as some other possible factors in each individual case, must be considered, has been known, though generally ignored, by chemists and other soil investigators. That the composition of the resulting solution with respect to the dissolved constituents remains constant so long as no one of the solid components disappears is well illustrated in a simple case—

by a mixture of sodium nitrate and potassium nitrate. If such a mixture be treated by successive portions of water, assuming of course that the temperature be kept constant, the composition of the several resulting solutions will be exactly the same so long as both solid salts remain in the mixture. Precisely the same sort of thing will happen with any mixture of solids, no matter how complex, and an interesting example has been under observation by this Bureau for several years.

A tract of land near Salt Lake City, Utah, has been under process of reclamation, tile drains having been installed and the land leveled and frequently flooded. When reclamation was undertaken, the surface soil of this tract contained, on the average, upward of 2.7 per cent soluble salts, while it now contains less than 0.3 per cent soluble salts. At frequent intervals since the installation of the drains, samples of the water from the outlet weir of the drainage system have been forwarded to the laboratory for analysis. The composition of the principal dissolved mineral constituents, at several different dates, are given in the following table:

TABLE I.—*Composition of soluble salts contained in the drainage water of the Swan tract.*

Date.	Ca.	Mg.	Na.	K.	SO ₄ .	Cl.	HCO ₃ .	CO ₃ .
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1902—September	0.38	0.50	33.74	2.04	18.62	37.76	6.49	0.48
October	.23	.78	34.73	1.49	19.14	39.52	5.06	.29
November	.19	.74	34.42	1.40	18.61	40.46	3.95	.23
1903—May	.38	.61	34.48	.84	29.90	38.19	4.30	.25
June	.45	.85	34.18	1.09	17.52	41.00	4.23	.42
July	.50	.80	34.06	1.25	18.24	40.24	4.67	.30
August	.35	.90	34.40	1.12	17.15	42.87	3.48	.16
September	.49	.72	34.54	1.24	17.31	42.02	3.36	.33
October	.47	1.02	33.43	1.52	16.08	43.28	3.33	.30
1904—January	.15	.75	33.93	1.26	20.08	36.64	6.94	.25
February	.34	.78	34.59	.70	18.95	40.15	4.49	
March	.29	.77	34.57	1.28	16.31	42.28	3.81	.19
April	.29	.70	34.28	1.37	20.93	38.04	3.33	1.06
May	.71	.74	26.92	4.01	21.26	40.93	4.05	1.38
June	.37	.70	32.60	3.55	19.94	37.42	4.05	1.37
August	.37	.86	33.85	2.13	17.12	41.31	3.20	1.16
September	.42	.79	34.10	1.35	19.01	39.85	4.11	.76
October	1.04	.60	33.01	1.86	21.42	36.63	4.68	.37
December	1.25	.70	32.62	1.69	19.89	37.44	6.18	.22
1905—February	.32	.67	33.59	.99	22.30	33.32	8.45	.36
March	.31	.66	33.46	1.30	21.60	33.86	8.46	.35
April	.35	.65	34.20	1.01	20.03	36.99	6.22	.55
May	.45	.86	33.43	1.20	20.59	36.04	6.96	.47
June	.40	.94	34.05	1.32	20.89	35.85	5.71	.84
July	.32	.69	33.67	1.30	21.17	34.94	7.23	.68
August	.35	1.04	33.12	1.58	21.58	35.92	5.72	.99
September	.42	.82	33.39	1.26	21.18	34.85	7.41	.67
1906—January	.55	.84	33.12	1.11	21.10	34.35	8.57	.36

It will be observed that the variations of the several constituents, within an interval of nearly four years, are very small, such differences as do appear being readily attributable to the relatively small changes in the actual concentrations of the drainage water at different times, produced by the addition of large quantities of water in flooding, some of which reached the tiles before coming to equilibrium with the soil components. Other similar examples might be cited, although no other field data are known to us which are as complete as in this case.

The data just presented is believed to be of more than ordinary importance, because it so well illustrates the character of the results which may be anticipated in a large number of cases in actual field-work. How long the practically constant percentage composition of the dissolved salts would continue in the drainage water under continued flooding it is, of course, difficult, if not impossible, to predict. It is reasonably certain that sooner or later some one or more of the solid components in the soil would be completely removed, barring absorption or some other special phenomena, and the nature of the solution might then be very materially altered. As a practical matter, however, it should be remembered that the persistence of the several solid phases of the alkali mixture does not necessarily mean that they are evenly distributed in the soil, and that while they may be determining the composition of the solution as it passes into the drain tiles, some of these solid phases may have been removed from the surface soil, which would then hold a solution of different character, in which latter crops could very well grow. This seems to be true in the case just cited, as there is evidence that crops can now be grown on the tract if proper cultural methods be maintained to prevent the subsequent capillary rise of the water added in flooding. It appears certain, however, that in such cases the land can not be truly regarded as finally reclaimed until the change in the composition of the drainage water shows that there has been a complete removal of some of the solid salts from that portion of the soil which feeds the drains. The analysis of the drainage water is the most ready method of following the changes taking place within the soil. That the nature of the drainage water and the changes which it may undergo are problems of great practical importance is obvious when it is considered that agricultural plants display such marked difference in their tolerance of different salts and salt mixtures in their nutrient media. It is also important to note that a study of drainage water not only furnishes a clue to the nature of the soil solution in the land from which it flows, but that it may have an important bearing on the management of neighboring lands upon which it may be desirable to use the water again for irrigation or where the land may be affected through seepage.

In order to obtain a clear idea of the mechanism of the chemical phenomena presented by these drainage waters, it will be necessary to consider the mutual solubility effects of one salt upon another, the various salts or molecular species which may be formed, the vapor pressure of the resulting solutions and the solids in contact with them, and the converse problem to that which has been considered above—i. e., the separation from solution of the salts which the dissolved constituents may form. Since calcium sulphate or gypsum is a predominating component in a large number of cases of alkali and determines their characteristics, it is convenient to take up the investigation from

the point of view of the solubility of this substance in aqueous solutions of other salts.

In considering the solubility of pairs of salts, there is one guiding principle commonly accepted—a result of the hypothesis of electrolytic dissociation—namely, that salts which yield a common ion mutually decrease each other's solubility, and that salts which do not yield a common ion increase each other's solubility. Exceptions are known, as for instance, the familiar one that sodium and potassium nitrate increase each other's solubility, while it is inconceivable that they could dissociate without the formation of a common ion.

Another interesting case is presented by magnesium sulphate and potassium sulphate, which mutually increase each other's solubility. Therefore, the indications of the dissociation hypothesis, however useful for purposes of classification, can not be accepted with confidence as general.

At a temperature of 25° C. the solubility of calcium sulphate in solutions of sulphuric acid presents a case similar to those just cited, in that increasing the quantities of sulphuric acid increases the solubility of the calcium sulphate up to a maximum point, after which further increase of the acid causes a decrease of the salt going into solution. It might be predicated here that in the more dilute solutions the dissociation of the sulphuric acid was of such a character as to yield HSO_4 ions rather than SO_4 ions, which alone it is possible to conceive the calcium salt as yielding. The evidence from studies of the transport number of sulphuric acid, as well as other considerations, rather decidedly negatives this supposition, however. With increasing concentration with respect to sodium, potassium, or ammonium sulphate the solubility of calcium sulphate does decrease, however, until a minimum point is reached, after which it steadily increases until some other solid than gypsum is also in contact with the solution. On the other hand, increasing concentration with respect to calcium nitrate or chloride steadily decreases the solubility of calcium sulphate as the fundamental hypothesis would require.

Increasing concentration with respect to the chlorides or nitrates of other bases than calcium causes an increase of the solubility of calcium sulphate, although in many cases a maximum solubility followed by a decrease is reached at some rather high concentrations, at which the indications of the dissociation hypothesis are not expected to hold. These higher concentrations are just those, however, which may reasonably be expected to occur in the crystallization of alkali salts and frequently, no doubt, in the leaching of them from the soil.

It is to be observed from the preceding paragraphs that no generalization exists from which the solubility of calcium sulphate in the presence of other salts could be satisfactorily anticipated, and the actual determination of the solubility curves for calcium sulphate in solutions

of other salts was necessary to a correct understanding of the case. A comparison of the curves that have so far been investigated shows that in general the basic constituents rather than the acid constituents have determined the solubility of the calcium sulphate and the character of the curves. If the curves be compared for the chlorides and the nitrates at 25° C., it will be found that the bases in the order of their reacting weights, excepting calcium, have had in both series an increasing effect on the solubility of the calcium sulphate.

As has been pointed out above, the presence of another salt in solution may have a marked influence on the form of the calcium sulphate. For instance, if calcium sulphate be precipitated from a solution saturated with respect to magnesium chloride at ordinary temperatures, it will separate as anhydrite, which is the most stable form under these conditions. But gypsum, the dihydrate, can exist in contact with a saturated solution of magnesium chloride, and its solubility has actually been determined in such a solution, probably because the rate of transformation to the more stable anhydrite is very slow. But if gypsum be brought into contact with a solution of potassium sulphate at 25° C. and maintained at a concentration higher than 32.5 grams per liter, the gypsum can not remain as such, but quite rapidly disappears, and a new solid, syngenite ($\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), separates from the solution. If, instead of potassium sulphate, the solution contain about 160 grams potassium chloride per liter, and be also saturated with respect to sodium chloride, gypsum can not remain in contact with it, but syngenite will again be formed. Similar cases involving other so-called "double sulphates" of calcium might be cited, and are described elsewhere in this bulletin. Just what double sulphates of calcium or what hydrates of calcium sulphate can exist could only be determined by empirical experimentation. But there is a rule which furnishes a guide as to that form which will persist in equilibrium with any given solution—namely, that form which has the vapor pressure nearest to, but not higher than, the vapor pressure of the solution. Should, however, two solids when mixed together have the same vapor pressure as a solution containing the same constituents as the solids, which, obviously, for any given temperature, could occur only at one definite concentration of the solution, then both solids and the solution can remain in contact in stable equilibrium. For instance, at 25° C. gypsum and syngenite can remain in stable equilibrium with a solution containing 32.5 grams potassium sulphate and 1.58 grams calcium sulphate per liter. But if the vapor pressure of the solution be slightly lowered, as by adding more potassium sulphate, then gypsum will disappear, leaving syngenite alone in contact with the solution. On the other hand, if the vapor pressure of the solution be increased, as by abstracting some of the dissolved potassium sulphate (or what amounts to the same thing, diluting the solution), then syngenite will disappear

and gypsum alone will be left in contact with the solution. This rule regarding the vapor pressures of solutions and the solids in contact with them is a special case of the more general principle of Le Chatelier, which may be stated thus: That any change from the outside of the system, disturbing any of the equilibrium factors, produces a corresponding reverse change within the system. There is always a tendency for the system to return to a condition of equilibrium accompanied by that particular change within itself which offers the least resistance to the external change imposed upon it. Increase of concentration induces the formation of that component or phase which tends to lower the concentration of the thing added; increase of temperature to the formation of that component or phase which absorbs the most heat; increase of pressure to the formation of that component or phase requiring the least volume; increase of vapor pressure to the formation of that component or phase which will most reduce the vapor pressure, etc. This general principle of Le Chatelier is of the utmost importance in considering complex systems, such as are presented by solutions in contact with salt mixtures, since through it the direction which changes in the system will take can not only be followed with certainty, but can, in the majority of cases, be readily predicted.

In considering such systems another useful generalization obtains which definitely describes the conditions of equilibrium. This is the phase rule. A *phase* is defined as any portion of a material system which is homogeneous, and a *component* is any constituent (or group of constituents) comprising the system, which may vary in concentration independently of every other component. Thus ice floating in water would be a system comprising one component, water, in three phases—liquid water, solid ice, and vapor. Gypsum in contact with water would be two components, water and calcium sulphate, in three phases—solid gypsum, liquid solution of calcium sulphate in water, and vapor.

In accordance with the *phase rule* a system containing n components, comprising $n + 2$ phases, can exist at but one temperature and one pressure, the composition of the phases being also definitely determined. If the system comprises $n + 1$ phases, it can exist over a range of pressure, or temperature, or concentration of some one or other of the phases. But arbitrarily fixing some one or other of these variables, for instance the temperature, the system again becomes completely and definitely determined. Likewise if the system comprises but n phases, it will be necessary arbitrarily to fix two of the possible variables in order to determine it definitely. For instance, if the system, gypsum in contact with a solution of potassium sulphate, be considered, there will be three components, namely, calcium sulphate, potassium sulphate, and water. At lower concentrations of

the solution there will be three phases, solid gypsum, liquid solution of potassium and calcium sulphates, and the vapor above the solution. There are, then, three components, in three phases. If we arbitrarily fix one condition, as, for instance, keeping the system at 25° C., it can still exist over quite a range of concentration of the liquid phase or range of vapor pressure of the system or range of osmotic pressure of the solution, and it would be necessary arbitrarily to fix one of these variable quantities also before the system becomes definitely fixed under equilibrium conditions. If the concentration of the liquid phase be gradually increased with respect to potassium sulphate a new solid phase, syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) will appear, and the system will then have three components in four phases, and it will be sufficient definitely to determine it under equilibrium conditions by arbitrarily fixing any one variable. Thus, if we again arbitrarily keep the system at 25° C. the concentration of the liquid phase will be 32.5 grams potassium sulphate and 1.58 grams calcium sulphate, respectively, per liter, and the system can only exist at 25° when the concentration of the solution is as just stated. For if the concentration be increased, as by adding a little more potassium sulphate (the vapor pressure of the solution being lowered thereby), gypsum (which has the higher vapor pressure) will disappear and syngenite alone will be the solid phase in contact with the solution. If, on the other hand, the concentration of the solution be lowered, as by adding a little more water, syngenite will disappear and gypsum alone will be the solid phase which persists. In either case the system is reduced to one of three components in three phases, and either solid by itself can remain in equilibrium with the solution over a considerable range of concentration of the solution.

Guided by these principles—the rule of Le Chatelier and the phase rule—it is possible to trace out the changes involved in the separation of several possible combinations of salts from even a very complex solution. This has been done with unusual completeness for those salts which comprise what is known as “white alkali.” Conversely, from this knowledge, together with the necessary data as to mutual solubility effects, it is possible to make precise statements as to the leaching effects of water on alkali soils, which are in many respects totally at variance with the notions which have hitherto prevailed. It must not be overlooked that absorption, selective absorption, flocculation, deflocculation, and surface effects enter into this last problem, and these may considerably modify the expected results in any particular case, but, barring such effects, the guiding principle in leaching experiments is that the composition of the drainage waters will change only when some one or more of the solid phases disappears.

While calcium sulphate as such is sometimes found in the soils of humid areas in noticeable amounts, no especial significance seems to

have been ascribed to it. As a mineral fertilizer it has generally been held to have a great value, and in its various forms, under the generic name of "land plaster," it is much used. Not only is it applied directly to the soil, but it is frequently applied with stable manures and composts to which it has been previously added, and it forms a very large part of the so-called "superphosphates" which have come into widespread use in recent years. It is, therefore, of obvious importance to have a knowledge of its solubility in pure water and in salt solutions in order to get an insight into how its use as a fertilizer may affect the character of the soil moisture, the great natural cultural medium from which plants draw their mineral nutrients.

In studying these problems much information of importance for other economic problems has been obtained. The setting of plaster of paris, much used in the arts, decorative work, and surgery, and the use of calcium sulphate in cements and in paper sizings, are dependent upon its relation to water and salt solutions. The use of water containing sulphates and calcium salts in boilers, with the formation of calcium sulphate boiler scale (probably the hemihydrate), and the formation of calcium sulphate pan coatings in the evaporation of the brines in salt works, are practical problems which have thus far largely defied a satisfactory treatment and can be intelligently attacked only on the basis of the facts brought out in the following pages.

The purpose of this bulletin is to bring together and arrange in a logical sequence the results of the numerous investigations which have been made on the relation of calcium sulphate to aqueous solutions. Experimental methods and details are either omitted or, if of unusual interest, are described but briefly, since the numerous references to the literature which are given will make them available to anyone who may be interested. In like manner practical applications of the results are merely indicated, as their discussion can be more profitably given elsewhere than in this necessarily technical description of a chemical problem.

TRANSFORMATIONS OF THE DIFFERENT MODIFICATIONS OF CALCIUM SULPHATE.

For a proper understanding of the solubility of calcium sulphate in water and in various aqueous solutions, it is necessary first to investigate the transformations which may take place in the degree of hydration of the solid and the crystalline forms in which the solid salt may appear. There are at least four well-defined forms,^a (1) gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, (2) the hemihydrate, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, (3) natural anhydrite, CaSO_4 , and (4) soluble anhydrite, CaSO_4 . The last two modifications have very different solubilities in water, the latter being more soluble than the natural anhydrite. Two other modifications of cal-

^aVan 't Hoff and Wilson, Sitzungsber, Akad. Wiss. Berlin, 1899, 599.

cium sulphate are claimed to exist by Rohland,^a namely, calcium sulphate obtained by heating the hemihydrate just above 130° C., and calcium sulphate obtained at a red heat. Both these modifications may be hydrated, i. e., will take up water to form gypsum, under proper conditions, e. g., by contact with a solution of one of the alkali sulphates,^b but they have no hydraulic properties and are therefore useless in the technical process of cementing. If, however, the heating takes place just above 525° C., there is a transformation into a modification quite similar to, if not the same as, soluble anhydrite, for it hardens very rapidly when it is moistened with water. Landrin^c has shown that the velocity of hydration of burnt gypsum depends on the time and on the temperature of burning, but he obtained results rather different from those of Rohland upon the hydraulic properties of gypsum which had been burnt at high temperatures.

The anhydrides formed by burning gypsum have been divided into two groups by Potilitzin,^d α -CaSO₄, burned between 120° and 200° , which takes up water readily and hardens, first forming the hemihydrate and then the dihydrate. The second modification, β -CaSO₄, is formed above 200° and does not harden, as water is taken up very slowly. The hemihydrate heated to 160° forms the α -modification, and at 350° the β -modification, while the hemihydrate is formed from gypsum at about 98° . Burnt gypsum must contain both modifications for good hydraulic properties, the hydrated compound formed from the α -modification filling in the spaces between the grains of the β -modification, which absorbs water but slowly.

The literature upon this subject, up to a few years ago, was quite bewildering and often contradictory, and consequently will be noticed rather briefly. The use of natural waters in steam boilers causes in many cases the formation of boiler scale, probably hemihydrate, which is a very poor conductor of heat and greatly reduces the efficiency of the engine. Johnston^e noticed that in a boiler working under a pressure of two atmospheres the scale analyzed according to the formula CaSO₄· $\frac{1}{2}$ H₂O. Rose^f ascribed the formula CaSO₄·H₂O to the substance which separated out from a sodium chloride solution carrying calcium sulphate. This solid lost one-third of its water when dried at 100° C., and in all probability was the hemihydrate. Million^g states that artificially prepared gypsum loses three-fourths of the water of

^a Zeit. anorg. Chem., **35**, 201 (1903).

^b Rohland, Zeit. anorg. Chem., **31**, 442 (1902).

^c Ann. Chim. Phys. (5), **3**, 433 (1874).

^d Jour. Russ. Phys. Chem. Soc., **25**, I, 207 (1893); **26**, 170, 221 (1894); **27**, 265 (1895).

^e Phil. Mag. (2), **13**, 325 (1838).

^f Ann. Phys., **93**, 606 (1855).

^g Ann. Chim. Phys. (3), **19**, 222 (1847); Compt. rend., **24**, 695 (1847).

crystallization at 80° to 85° , while the natural gypsum undergoes the same change at 105° to 110° . The last half molecule of water is driven off above 200° . Plessy,^a however, finds that both natural and artificial gypsum undergo the first change at about 110° . Million's contention is rather confirmed by experiments of later date by Zeidler.^b According to Lacroix,^c the first change takes place at 80° to hemihydrate and at 125° to anhydrite, and according to Guether^d gypsum is completely dehydrated at 110° . The changes which gypsum undergoes at higher temperatures in sealed tubes have been investigated by Hoppe-Seyler,^e who found that gypsum changes to the hemihydrate at 140° C., and in the presence of a saturated solution of sodium chloride the change takes place at the lower temperature of 125° . Solutions of calcium chloride also reduce the temperature at which the transformation takes place. Under all circumstances the hemihydrate spontaneously changed rather readily into one of the anhydrous forms.

The formation of anhydrite has been investigated in the presence of salts which do not give up their water of crystallization readily. Pošepný^f has found that anhydrite is formed from gypsum in the presence of such salts as calcium chloride and magnesium chloride. The results of Hoppe-Seyler have been confirmed by Rose,^g who showed that gypsum lost water at even as low a temperature as 100° . At lower temperatures, however, gypsum always separated out from sodium chloride solutions, a result which has been confirmed by Hoppe-Seyler^h in a later publication. These statements are contested by Roth,ⁱ who found anhydrite deposited from sodium chloride solutions at ordinary temperatures. The results of Spezia^j indicate that anhydrite separates from a saturated sodium chloride solution at a pressure of 500 atmospheres, in spite of the fact that gypsum occupies one-eleventh less volume than the anhydrite and water resulting from the decomposition.

Vater^k has evaporated at ordinary temperature these solutions, all of which contained calcium sulphate, viz, saturated sodium chloride, a solution containing sodium chloride and magnesium chloride in the same proportion as they are present in sea water, and a saturated magnesium chloride solution. In all cases he found that the new

^a Compt. rend., **24**, 658, 812 (1847).

^b Dingl. Poly. Jour., **180**, 471 (1866).

^c Compt. rend., **126**, 360, 553 (1898).

^d Ann. Chem., **218**, 297 (1883).

^e Ann. Phys., **127**, 161 (1865).

^f Verh. d. k. k. geol. Reichanst., 1869, 140.

^g Ann. Phys., **145**, 177 (1872).

^h Zeit. deutsch. geol. Gesell., **27**, 495 (1875).

ⁱ Sitzungsber. Akad. Wiss. Berlin, 1879, 89.

^j Zeit. Kryst., **13**, 302 (1888).

^k Sitzungsber. Akad. Wiss. Berlin, 1900, 269.

crystals were gypsum, while natural anhydrite, when placed in these solutions, remained unchanged. From these results it is impossible to come to any definite conclusion regarding the stable solid phase, and as the results of van 't Hoff and his coworkers have shown conclusively that the rate at which stable equilibrium is reached is exceedingly slow, it is improbable that Vater realized equilibrium conditions.

The investigations of van 't Hoff^a and his coworkers have been conducted by somewhat different methods from those which have been cited in the foregoing paragraphs. The temperatures of transformation of one form into another have been obtained by dilatometric and tensimetric measurements. The criterion of the stability of any hydrate in the presence of a solution is that its solubility in the solution shall be less than the solubility of the other hydrates or of the anhydrous forms of the salt. This criterion may also be expressed in terms of vapor pressures, thus: The vapor pressure of the stable form in contact with any other modification of the salt must be lower than the vapor pressure of the solution in equilibrium with it. As soon as a temperature is reached at which the vapor pressure of the hydrate becomes greater than that of the solution in equilibrium with it, there is a change from that solid phase to the one which possesses the next lower vapor pressure. Using this principle as a guide, van 't Hoff and Armstrong^b have determined at different temperatures the vapor pressure at which both the dihydrate and the hemihydrate^c can exist in equilibrium, or, in other words, the vapor pressure of a mixture of these two salts at the temperature of the experiment. If to this mixture there is added a solution having a greater vapor pressure all the hemihydrate will change into the dihydrate, but if a solution of a less vapor pressure, the hemihydrate will become the more stable form. Thus, to find the inversion temperature and pressure of any solution it is sufficient to plot on a diagram the vapor-pressure curve representing the transformation of gypsum to the hemihydrate and the vapor-pressure curve of the solution. The point of intersection at which the vapor pressure of the solution becomes less than the vapor pressure of gypsum in the presence of the hemihydrate is the inversion temperature. From data given by Lescoeur,^d Donnan,^e and from their own measurements, van 't Hoff and Armstrong^f have

^aZeit. phys. Chem., **45**, 257 (1903).

^bSitzungsber. Akad. Wiss. Berlin, 1900, 559.

^cThe hemihydrate for these experiments was prepared by van 't Hoff and Armstrong by mixing 50 c. c. of nitric acid (sp. gr.=1.4) with 20 grams gypsum and keeping the mixture at 40° for eighteen hours. At the end of this time the resulting solid phase was washed with alcohol and dried quickly. The solid, upon analysis, showed 6.23 per cent H₂O, which agrees with the formula CaSO₄·½H₂O.

^dRecherches sur la dissociation des hydrates salines, 1888, 115.

^eAnn. Chim. Phys. (6), **21**, 511 (1890).

^fLoc. cit.; also van 't Hoff, Zeit. Elektrochemie, **8**, 575 (1902).

computed the vapor pressures of gypsum in the presence of the hemihydrate at temperatures from 0° to 110° C. in 5° intervals.

These results are given in Table II, in which are given the vapor pressures of water, of a saturated solution of magnesium chloride,

and of a saturated solution of sodium chloride. The actual composition of these solutions will not be constant, of course, as the solubility of the salts varies with the temperature. The table also gives the vapor pressure of gypsum in contact with one of the other modifications of calcium sulphate, since the vapor pressure of gypsum depends on the modification with which it is in contact. The symbol t_u signifies the temperature above which gypsum can not exist in equilibrium with the other modification of calcium sulphate; for, above this temperature the vapor pressure of gypsum in contact with the second modification would be greater than the solution saturated with this modification. This state of affairs is quite analogous to the case of Glauber's salt changing at 32.8° C. to anhydrous sodium sulphate. Above this temperature the vapor pressure of

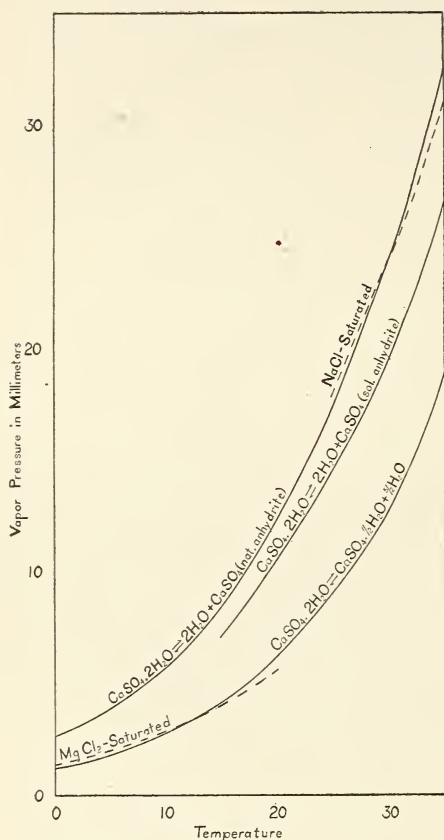


FIG. 1.—Vapor pressure curves (0° to 35° C.).

Glauber's salt in contact with anhydrous sodium sulphate is greater than that of the solution saturated with anhydrous sodium sulphate, and therefore Glauber's salt changes into the solid anhydrous sulphate and its saturated solution.

TABLE II.—Vapor pressure of gypsum in contact with different solids and solutions.

Temperature.	Water.	Saturated solution—		Gypsum in equilibrium with—		
		MgCl ₂ .6H ₂ O.	NaCl.	Hemihydrate.	Soluble anhydrite.	Natural anhydrite.
°C.	mm.	mm.	mm.	mm.	mm.	mm.
0	4.57	1.34		1.17		2.62
5	6.51	1.96		1.84		3.93
10	9.14	2.82		2.78		5.79
15	12.7	4.0		4.21	7.0	8.43
20	17.4	5.6		6.24	10.7	12.2
25	23.5	7.76		9.1	14.5	17.2
30	31.5		17.7	12.7	19.4	24
35	41.8		31	18.7	26.5	32.2
40	54.9		40.8	26.3	34	45.4
45	71.4		53	36.4	47.2	61.4
50	92		68.3	50	61.5	87.2
55	118		87.3	68	84	109
60	149		111	91.4	108	143
65	187		139	122	140	<i>t_u</i> =66°
70	233		173	161	185	
75	289		214	210	242	
80	355		263	272	314	
85	433			350	407	
90	526			446	<i>t_u</i> =89°	
95	634			565		
100	760			711		
105	906			888		
110	1,075			<i>t_u</i> =107°		

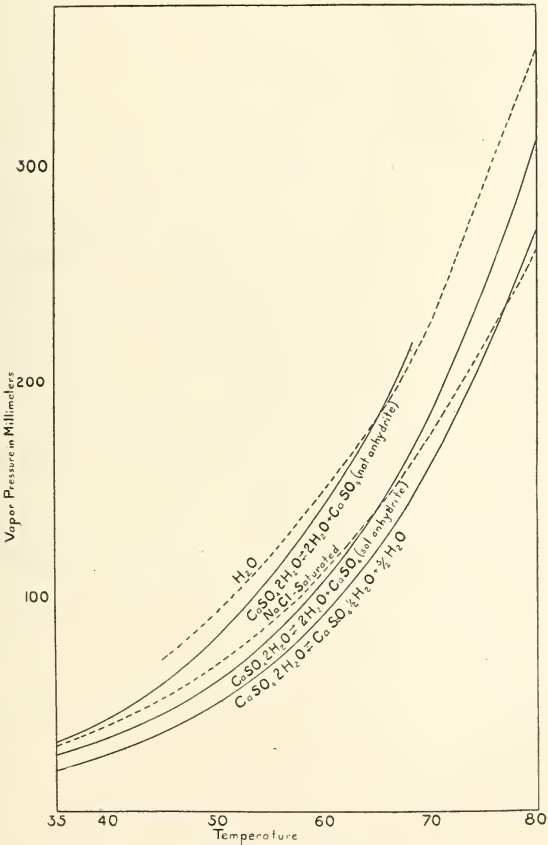


FIG. 2.—Vapor pressure curves (35° to 80° C.).

The vapor pressure for water is shown in figures 1, 2, and 3, and making the assumption that the small amount of calcium sulphate present in the solution does not materially alter the vapor pressure of water, the intersection of the two curves gives the inversion temperature. This temperature was found to be 107°C . and the pressure

970 mm. This result was confirmed by a study of the changes in volume of a mixture of the dihydrate and the hemihydrate in a dilatometer. At 107.75° the level of the mercury rose 6 mm. per hour, and at 106.75° the level of the mercury fell 2 mm. per hour. This indicates that the inversion temperature is very close to 107° . Portions of vapor pressure curves of some solutions have been given by van 't Hoff and Armstrong, and from these it is possible to determine the inversion temperature in the presence of salt solutions of these concentrations.

Table III indicates that the inversion temperature of gypsum to hemihydrate in the presence of a saturated solution of sodium chloride is about 76° , in good accord with the experimental result of van 't Hoff and Wilson at 77.1° . For some other sodium chloride solutions the data are given in Table III. It indicates that the inversion temperature in the presence of a 20 per cent sodium chloride solution is about 93° , a result in good accord with the solubility results

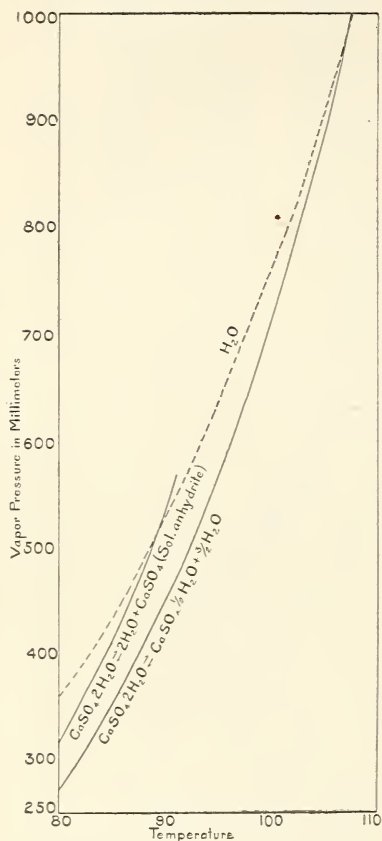


FIG. 3.—Vapor pressure curves (80° to 110°C .).

obtained by Tilden and Shenstone, which will be discussed later. It indicates also that in the presence of a $3\frac{1}{2}$ per cent solution of sodium chloride, which is about the composition of sea water, the inversion temperature is about 105° .

TABLE III.—*Vapor pressure of solid gypsum and of solutions in contact with it.*

Temperature.	Saturated solution of sodium chloride.		Temperature.	20 per cent solution of sodium chloride.		Temperature.	3½ per cent solution of sodium chloride.	
	Gypsum.	Solution. ^a		Gypsum.	Solution.		Gypsum.	Solution. ^b
° C.	mm.	mm.	° C.	mm.	mm.	° C.	mm.	mm.
75	210.2	214.0	90	446.3	462.0	100	710.8	744.0
80	272.4	263.3	95	564.8	556.7	105	887.8	887.4

^a Nicol, Phil. Mag., (5), 22, 502 (1886).^b Wüllner, Ann. Phys., **103**, 529 (1858); Tammann, Mém. de l'acad. de St. Petersburg, (7), **35**, No. 9.TABLE IV.—*Vapor pressure of solid gypsum and of solutions in contact with it.*

Temperature.	Saturated solution of calcium chloride.		Temperature.	15 per cent solution of calcium chloride.		Temperature.	Saturated solution of magnesium chloride.	
	Gypsum.	Solution.		Gypsum.	Solution. ^a		Gypsum.	Solution.
° C.	mm.	mm.	° C.	mm.	mm.	° C.	mm.	mm.
15	4.21	4.536	100	710.80	712.00	10	2.78	2.82
20	6.24	5.616	105	887.80	851.00	15	4.21	4.00

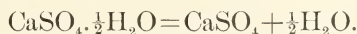
^a Wüllner, Ann. Phys., **103**, 529 (1858).

Table IV indicates that for a saturated solution of calcium chloride the inversion temperature is about 17° and for a 15 per cent solution of calcium chloride about 100°, in accord with the solubility determinations of Tilden and Shenstone, which is discussed on page 48. In the presence of a saturated magnesium chloride solution this inversion takes place as low as 11° C.

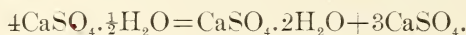
The conditions under which gypsum can exist in the presence of the soluble anhydrite have been studied by van 't Hoff, Hinrichsen and Weigert.^a According to Le Chatelier^b this transformation takes place at 163°. Evidence of this change could not be observed by the former experimenters, although they do not deny the possibility of a phenomenon such as Le Chatelier describes. They have found that the change from gypsum to soluble anhydrite does not occur above 107°, as would be expected, but was found to take place below that temperature. Gypsum was placed in a dilatometer with a saturated sodium chloride solution and was heated to 76°. At that temperature an expansion in volume occurred, due to the reaction



When the dilatometer was cooled down again, the reverse process of contraction did not take place, and on cooling to 50° a considerable further expansion in volume took place, due to the reaction

^a Sitzungsber. Akad. Wiss. Berlin, 1901, 570.^b Recherches expérimentales sur la constitution des mortiers hydrauliques, 1887-88.

That is, anhydrite is stable at a lower temperature than the hemihydrate in the presence of a saturated sodium-chloride solution. The temperature at which gypsum and this anhydrite (soluble) can exist in equilibrium has been found by van 't Hoff, Hinrichsen, and Weigert, by the same method as was adopted in studying the equilibrium between gypsum and the hemihydrate. This temperature is very close to $89^{\circ}\text{C}.$, and therefore above that temperature gypsum changes into soluble anhydrite. As the formation of anhydrite from gypsum takes place at a lower temperature than the formation of the hemihydrate from gypsum, it follows that the hemihydrate must be metastable at all temperatures, and must change according to the equation



This explains the loss of hardening powers by commercial gypsum (hemihydrate), which when freshly burned requires more water to harden than does gypsum which has been allowed to stand for some time. The influence of other compounds upon the rate at which this reaction takes place has been investigated by Rohland,^a but the results of this work are of a qualitative nature.

Still a second modification of anhydrous calcium sulphate is known—the anhydrite found in nature. By long contact of the soluble anhydrite with boiling water van 't Hoff and Weigert^b have shown that the solubility decreases, but that there is no change in the chemical composition of the solid phase, as the natural anhydrite is more stable than either the soluble anhydrite or the hemihydrate. The temperature of formation from gypsum must be lower than that of either of the other forms, and consequently the vapor pressure of gypsum in contact with natural anhydrite will be greater than that of gypsum in contact with either of the other modifications.

The vapor pressures at which gypsum changes to the natural anhydrite at different temperatures has been given in Table II. The temperature at which this vapor pressure curve cut the vapor pressure curve of water is $66^{\circ}\text{C}.$, the temperature at which anhydrite, gypsum, and aqueous solution exist in equilibrium. The temperature at which the former vapor pressure curve cuts that for saturated sodium chloride solution is the temperature of the transformation in the presence of this solution. From the diagram (fig. 1) this is found to be at 30° and the pressure is 24 mm. This agrees with dilatometric measurements made at temperatures in this neighborhood. Above this temperature there was an expansion because the products of the change (anhydrite and solution) occupy greater volume than gypsum; below 30° the reverse changes take place. This is also in harmony with the

^a Zeit. anorg. Chem., **35**, 194 (1903).

^b Sitzungsber. Akad. Wiss. Berlin, 1901, 1140.

statement of Fassbender^a that gypsum is the stable phase in equilibrium with cold saturated sodium chloride solutions, while at higher temperatures anhydrite is the stable phase. The results of Hoppe-Seyler,^b who obtained natural anhydrite at 125° from saturated sodium chloride solution, are not inconsistent with the results of van 't Hoff, Hinrichsen and Weigert. Using a saturated sodium bromate solution the inversion temperature was found by the latter investigators to be 50.2° C. at a pressure of 83.3 mm. The formation of natural anhydrite at ordinary temperatures by saturated calcium chloride and saturated magnesium chloride solutions, as given by Brauns,^c is in accord with the above observations. Struve^d has found that in the presence of concentrated sulphuric acid (of which the vapor pressure is very low) the stable solid phase is the natural anhydrite.

To summarize the data upon the changes of the different forms of calcium sulphate, there exist but two forms of this salt which are stable in the presence of any solution—gypsum and natural anhydrite—and the conditions under which one or the other form is stable depend upon the temperature and the nature of the solution with which it is in contact. For a calcium sulphate solution this inversion temperature is about 66°, for a saturated sodium bromate solution the temperature is 50°, and for a saturated sodium chloride solution the temperature is 30°. To determine the inversion temperature for any other salt solution it is necessary merely to draw its vapor pressure curve, and assuming that the calcium sulphate which goes into solution does not materially alter this vapor pressure, the point of intersection of this curve with the curve representing equilibrium conditions between natural anhydrite and gypsum will indicate the proper temperature. The other two forms—soluble anhydrite and the hemihydrate—are always metastable, and the conditions under which gypsum changes into either one will be determined from the intersection of the proper vapor pressure curves.

CALCIUM SULPHATE IN NATURE.

The facts that natural anhydrite is more stable than soluble anhydrite and that soluble anhydrite is more stable than the hemihydrate are of great importance in explaining the existence in nature of the natural anhydrite. As the temperature at which gypsum changes into the natural anhydrite was formerly considered to be over 150° C., there seemed to be no explanation of the presence of anhydrite in natural deposits. This temperature has been shown to be 66° in the presence of water, and even as low as 30° in contact with saturated sodium

^a Ber., **11**, 1968 (1878).

^b Ann. Phys., **127**, 161 (1866).

^c Neues Jahrb. f. Min., 1894 (2), 257.

^d Zeit. Chem., **5**, 324 (1869).

chloride solution. Further, it is highly probable that anhydrite has been deposited from solutions which have contained large quantities not only of common salt but also of other very soluble salts, all of which have tended to depress the inversion temperature. Just as the presence of anhydrite in salt regions was inexplicable, so the absence of the hemihydrate proved very perplexing. This, however, agrees perfectly with the data which have been determined by van 't Hoff and his coworkers. The hemihydrate and soluble anhydrite are under all conditions metastable in contact with solutions and tend to change into the stable forms natural anhydrite and gypsum.

In this connection it is interesting to note that a state of affairs somewhat similar to that just described for calcium sulphate exists in the case of the modifications of calcium carbonate, calcite, and aragonite. Becquerel^a has observed that in the presence of a fairly concentrated potassium carbonate solution, a crust of aragonite crystals were deposited after several years' contact. Calcium carbonate when deposited from solutions containing sodium chloride or ammonium chloride below 30° has been found by Watson^b to crystallize as calcite, but above that temperature as aragonite.

The only two modifications of calcium sulphate found in nature are, as might be expected, natural anhydrite and gypsum, the stable forms. Both these minerals are found in large quantities, widely distributed. Gypsum^c occurs near Lockport, at Camillus, Manlius, and Troy, N. Y.; in Davidson County, Tenn.; at St. Marys, Md.; at Poland and Canfield, Ohio; in Mammoth Cave, Kentucky; in New York State from Syracuse to the western extremity of Genesee County; in Michigan, Illinois, Virginia, Tennessee, Kansas, Arkansas, Texas, Iowa, Nevada, California, Wyoming, Oregon, Colorado, Montana, Dakota, Oklahoma, New Mexico, and Arizona; also at Hillsboro, New Brunswick, and in Hants, Colchester, and other districts in Nova Scotia. In Europe gypsum is found at Bex in Switzerland, at Hall in the Tyrol, Sicily, at Montmartre near Paris, at Castelino near Leghorn, and in many other localities. Anhydrite is found with gypsum at Lockport, N. Y.; near Windsor, Nova Scotia, and at Hillsboro, New Brunswick. It has been discovered also in salt mines near Hall in Tyrol, and at Bex, Switzerland; at Sulz on the Neckar, Würtemberg; Himmelsberg near Ilfeld; Bleiberg, Carinthia; Lüneburg, Hanover; Lauterberg in the Harz; Kapnik, Hungary; Ischl, Austria; Aussee, Styria; Berchtesgaden, Bavaria; at Rienthal and other localities in the Alps, and at Stassfurt.

^a Compt. rend., **76**, 245 (1873).

^b Chem. News, **63**, 109 (1891).

^c See Dana, *A System of Mineralogy* (1868), pp. 621, 637; Adams et al., *Gypsum Deposits of the United States*, U. S. Geol. Survey Bul. No. 223 (1904).

The conditions under which the gypsum and anhydrite have been deposited are indicated in the preceding chapter. A deposition of calcium sulphate from a strong solution of salts is in the form of anhydrite, and a crystallization at higher temperatures from more dilute solutions also yields anhydrite. Anhydrite is the first compound crystallizing out of the evaporating saline solution from which the Stassfurt salt beds resulted. Bischof^a has divided these beds vertically into four regions, of which the first is known as the anhydrite region.^b After the deposition of anhydrite and its exposure to weathering influences, or after the mother liquor has for any reason been drained off,^c there is a tendency to form gypsum. This formation has been observed in process^d at Bex in Switzerland, where extensive beds are altered in part to gypsum to a depth of 60 to 100 feet, below which unaltered anhydrite is found. Sometimes specimens of anhydrite are altered between the folia or over the exterior. These facts have long been known, as is shown by the following quotation from Bischof's Chemical and Physical Geology.^e

When the gypsum has been examined at somewhat greater depths it is found to be no longer hydrated, but occurs in the anhydrous state as anhydrite. This leads to the conjecture that gypsum is in great part formed from anhydrite by contact with the atmosphere. It is not surprising that this action should extend to greater depths in some places when the masses of rock are much fissured and torn asunder, thereby allowing a free ingress to the atmospheric air.

Blum mentions several places where a conversion of anhydrite into gypsum has taken place, and, among others, the valley of Canaria, in Switzerland. In this locality the anhydrite, where it comes to the surface, is converted over a wide extent into gypsum. At Bex, according to the observations of V. Charpentier, all the gypsum which occurs upon the surface has arisen by conversion of anhydrite. There are pieces, indeed, in which the transition can be traced. The pure anhydrite is found always in the inner parts of the rock or in the steep parts where, by means of landslides, the interior of the rock has been exposed. Similar appearances have been observed by Alberts in the *muschelkalk* of the southwest of Germany.

Anhydrite takes up, during its conversion into gypsum, about one-fourth its weight of water. If its specific gravity were not thereby altered, its volume would only undergo an increase proportional to the amount of water taken up. But since the

^a See Dana, loc. cit., p. 641.

^b The following description of the Stassfurt salt deposits is from Ries's "Economic Geology of the United States" (1905), p. 127.

At the bottom is the main bed of rock salt, which is broken up into layers 2 to 5 inches thick by layers of anhydrite. Above this comes 200 feet of rock salt, with which are mixed layers of magnesium chloride and polyhalite. Resting on this is 180 feet of rock salt, with alternating layers of sulphates, chiefly kieserite, the sulphate of magnesia. These layers are about 1 foot thick. Lastly, and uppermost, is a 135-foot bed consisting of a series of reddish layers of rock salts of magnesia and potassium, kainite, kieserite, carnallite, tachydrite, as well as masses of snow-white boracite.

^c This has actually taken place in some of the gypsum deposits of Kansas. See Haworth, Mineral Resources of Kansas, 1897, p. 61.

^d See Dana, loc. cit., p. 622.

^e 1853 ed., p. 422.

specific gravity of gypsum is only four-fifths of that of anhydrite, the volume must on this account, also, increase during the conversion. The expansion of anhydrite during its transformation into gypsum must, therefore, be very considerable. Its effects are very well seen in old galleries of mines which have been formed in anhydrite. In these there occur parts of the walls so loosened that the miners can scarcely pass.

SOLUBILITY OF CALCIUM SULPHATE IN WATER.

The solubility of gypsum in water has been investigated by many experimenters. The experimental results published prior to 1870 are, however, of little value, for they do not agree with one another, nor do they agree with measurements made more recently and with greater precision. The first series of accurate results on the solubility of gypsum in water was obtained by Marignac,^a who worked with much greater care than the earlier experimenters.^b His results agree quite closely with the more modern results. Droeze^c several years later determined the solubility of gypsum at temperatures ranging from 0° to 35° C., over which Marignac had obtained but few measurements. By the method of least squares Droeze calculated the most probable values for the solubility, taking into consideration his own and Marignac's results. These values are given in Table V.

TABLE V.—*Number of parts of water sufficient to dissolve one part of gypsum at different temperatures, as determined by Droeze and Marignac.*

Droeze.		Marignac.			
Temper- ature.	Parts water.	Temper- ature.	Parts water.	Temper- ature.	Parts water.
° C.		° C.		° C.	
0	415	40	369	80	404
5	412	45	372	85	415
10	407	50	374	90	427
15	398	55	375	95	440
20	371	60	377	100	455
25	365	65	381		
30	361	70	387		
35	359	75	395		

The results of Raupenstrauch,^d published in 1885, also agree very well with the latest results on this subject. The next series of measurements were by Goldammer,^e who found that complete saturation

^a Arch. Sciences phys. et nat., Genève, 1873, No. 190.

^b Henry, Jour. Phar., **12**, 31 (1826); Poggiale, Ann. Chim. Phys. (3), **8**, 463 (1843); Lassaigne, Jour. Phar. (3), **5**, 301 (1844); Buchholz and Giese, Gmelin's Handbuch., 5th edn. (1853), p. 186; Tipp, Vierteljahrsschrift f. prakt. Pharmacie, **3**, 506 (1854); N. Jahrb. Phar., **2**, 375 (1854); Bischof, Lehrbuch Chem. Phys. geol., 2d edn., II, p. 184; de Boisbaudran, Ann. Chim. Phys. (4), **9**, 173 (1868); (5), **3**, 477 (1874); Church, Zeit. Chem., **3**, 735 (1867); Bul. Soc. Chim. (2), **9**, 308 (1867); Cossa, Gazz. chim. ital., 1873, 135, et al.

^c Ber., **10**, 330 (1877).

^d Monatsh., **6**, 563 (1885).

^e Phar. Centralhalle, **29**, 193 (1888).

could be effected by shaking precipitated gypsum with water for five minutes. Hulett and Allen^a have determined the solubility of gypsum with great precision and their results have an especial value, as will be shown presently. The solubility at 25° of powdered calcium sulphate and gypsum from a number of sources has been determined in this

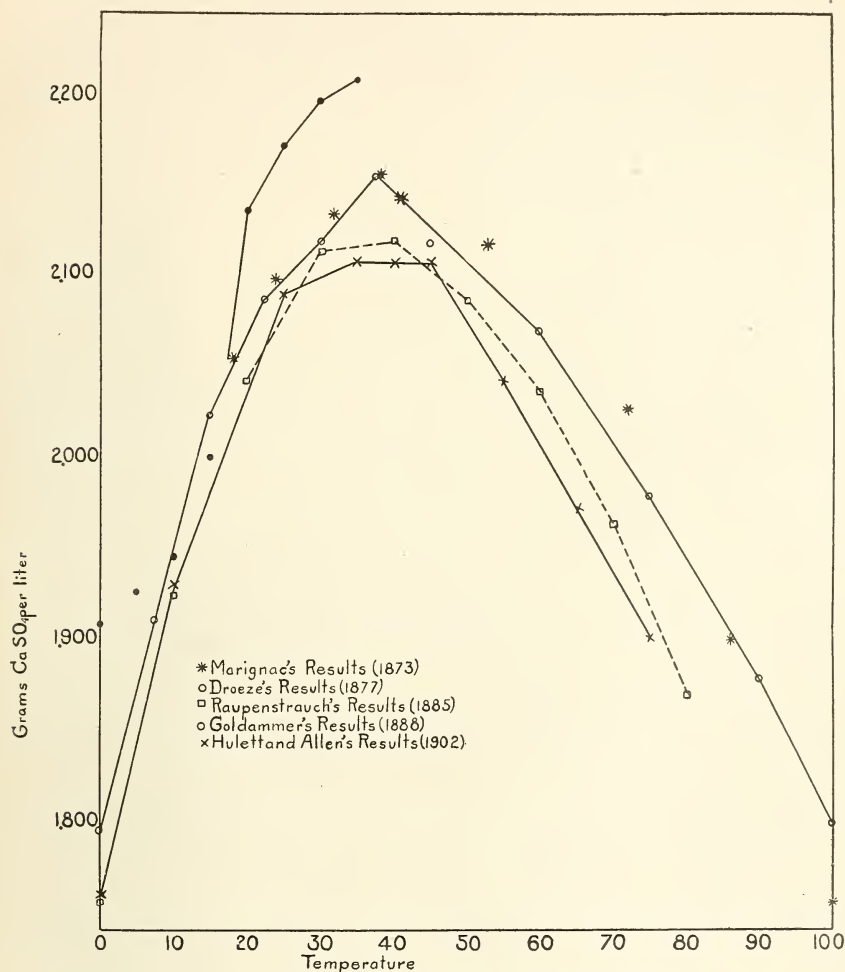


FIG. 4.—Solubility of calcium sulphate in water (0° to 100° C.).

laboratory^b with concordant results. The results of these investigations have been recalculated in order to compare the data, and the only basis on which such a comparison could be made was to find the ratio of parts of gypsum (CaSO_4) to water. All the earlier work gives the results in this form without recording the densities of the solutions.

^a Jour. Am. Chem. Soc., **24**, 667 (1902).

^b Cameron and Breazeale, Jour. Phys. Chem., **7**, 571 (1903).

Hulett and Allen's results are given as grams of CaSO_4 per 100 c. c. of solution and from the density determinations the number of grams of CaSO_4 per 100 grams of water have been calculated. The results of Hulett and Allen are given in the foregoing diagram (fig. 4) taken from their paper.

The reason for the wide discrepancies in all the earlier work seems to be the tendency to form solutions supersaturated with respect to the solid phase $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This may be attributed to two causes—the uncertainty in the earlier work as to the nature of the solid phase in contact with the solution, and the variation of the solubility of calcium sulphate depending on the size of the particles of the solid phase.

It is generally true that when a salt forms several hydrates the hydrate in stable equilibrium with a solution of the salt is that one which exists in equilibrium with the weakest solution. For instance, below 33°C . a solution saturated with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is less concentrated than the solution saturated with respect to the anhydrous salt, and therefore the hydrated salt is the stable compound. Above 33° the reverse is the case and the anhydrous salt is the stable form in contact with a solution. In the present case of calcium sulphate, there are (1) the anhydrous salt CaSO_4 (anhydrite), (2) the hemihydrate $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$, and (3) the dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum).

TABLE VI.—*Solubility of calcium sulphate in water.*

Temperature.	Grams CaSO_4 per 1,000 grams water, according to—					
	Marignac.	Droeze.	Raupenstrauch.	Goldammer.	Hulett and Allen.	Böttger. ^a and Breazeale.
$^\circ \text{C}$.						
0	1.906	1.906	1.756	1.795	1.759	
5		1.924				
7.5				1.909		
10		1.943	1.922		1.928	
15		1.997		2.020		
18	2.051				2.019	
20		2.132	2.039			2.036
22.5				2.083		
24	2.093					
25		2.167			2.086	2.126
30		2.192	2.109	2.114	2.098	
32	2.129					
35		2.203			2.104	
37.5				2.150		
38	2.150					
40			2.115		2.102	
41	2.138					
45				2.114	2.103	
50			2.083			
53	2.112					
55					2.038	
60			2.032	2.066		
65.3					1.969	
70			1.960			
72	2.023					
75				1.976	1.898	
80			1.868			
86	1.898					
90				1.876		
99	1.754					
100				1.798		

^a Zeit. phys. Chem., 46, 603 (1903).

The boiling point of the solution in equilibrium with gypsum has been determined by van't Hoff and Armstrong^a as 101.45° C. at atmospheric pressure. The vapor pressure curves for gypsum and for the solution saturated with gypsum have been determined by these experimenters, and thus the transition temperature of gypsum has been found. For stable equilibrium the vapor pressure of the solid hydrate must be less than the vapor pressure of the solution in equilibrium with it. The stable hydrate under these conditions is that hydrate which has the highest vapor pressure or the hydrate with the greatest degree of hydration, the vapor pressure being, of course, lower than that of the solution. The vapor pressure of gypsum becomes greater than that of the solution in equilibrium with it at 107° C., and therefore there is a change in the solid phase, the lower hydrate $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$ making its appearance. The effect of other salts in solution upon the transition temperature will be considered in another place. The rate at which anhydrite passes into aqueous solution has been shown by McCaleb^b to be much slower than that at which gypsum goes into solution, although its solubility at lower temperatures must be greater, as gypsum is the stable phase and therefore the least soluble. This fact explains the extremely slow rate at which anhydrite changes over into gypsum in the presence of water. The velocity at which the final equilibrium is reached, when the hemihydrate is shaken with water, seems to be rather slow, and consequently, unless equilibrium is attained, the observed concentration of the solution is greater than that of the solution saturated with gypsum. This tendency to supersaturation has been found by Goldammer^c to be greatest at ordinary temperatures. Gypsum which had been dried at 120°–130° to constant weight and dissolved in water has been found by Erlenmeyer^d to possess a high solubility, which decreased after some days to the normal solubility of gypsum in water. His results follow:

10 minutes after adding burnt gypsum to water, 1 part CaSO_4 in 82 parts water.

20 minutes after adding burnt gypsum to water, 1 part CaSO_4 in 170 parts water.

2 days after adding burnt gypsum to water, 1 part CaSO_4 in 391 parts water.

14 days after adding burnt gypsum to water, 1 part CaSO_4 in 495 parts water.

During this time there has been a change in the crystalline structure of the solid from burnt gypsum to that of ordinary gypsum. Practically the same results have been obtained by Marignac^e and by Potilitzin.^f

The second reason for the abnormally high solubility found for

^a Sitzungsber. Akad. Wiss. Berlin, 1900, 559.

^b Am. Chem. Jour., **11**, 31 (1889).

^c Phar. Centralhalle, **29**, 193, 215 (1888).

^d Verhandl. Math. phys. Classe K. bayer. Acad., 1872, 269.

^e N. Arch. ph. nat., Genève, **48**, 120 (1873).

^f Jour. Russ. Phys. Chem. Soc., **25**, 207 (1893).

gypsum by the earlier experimenters has been demonstrated by Hulett and Allen.^a The solubility of gypsum depends on the size of the particles in contact with the solution, particles less than 0.3 micron in size giving a solution 20 per cent more concentrated than a solution in equilibrium with massive gypsum. This is attributed to the influence of surface tension on the solubility, for Hulett^b has shown that the energy on the surface bounding a solid and its saturated solution is a measurable factor of the solubility. The concentration of the solution in equilibrium with a curved surface is different from that in equilibrium with a plane surface, a convex surface having a greater solubility and a concave one a less solubility than a plane surface. A finely powdered surface will, therefore, possess a greater solubility than the same substance in mass. In order to obtain a "normally saturated solution"—i. e., a solution in equilibrium with a plane surface of the solid—it is sufficient to allow all the finer particles to dissolve, as they are more soluble, and then to precipitate again on the less soluble larger pieces.

The experiments of Hulett and Allen, in which water was made to flow over plates of gypsum, must be taken as giving most nearly the true value of the solubility, although not the value which would be obtained under ordinary conditions. The curve of solubilities found by Hulett and Allen shows a maximum solubility at 40° C. The reasons for this maximum have been sought by these authors, and it has been connected with the change in the heat of solution at this temperature; but the reason why either of these correlated quantities, heat of solution and solubility, should undergo a change is still unexplained. It was thought that there was a change of solid phase at this temperature, but the vapor pressure curve of gypsum shows no break up to 107° C., at which temperature gypsum changes to the hemihydrate. This regularity excludes the explanation of the appearance of a new solid phase.

SOLUBILITY OF CALCIUM SULPHATE IN AQUEOUS SOLUTIONS.

The solubility of calcium sulphate in different solutions has been measured by a large number of investigators, and it has been considered advisable to collect all the available data on this subject for the sake of comparison. As there is a general theory that the effect of another substance in solution which yields a common ion should depress the solubility, it is convenient to divide the different solutions into three general classes: First, containing solutes which yield an ion

^a Loc. cit.

^b Zeit. phys. Chem., **37**, 385 (1901). The effect of the size of solid particles has been shown by Ostwald [Zeit. phys. Chem., **34**, 496 (1900)] to have an influence on the solubility. Thus he found that the solubility of very finely divided mercuric oxide is greater than that of coarse mercuric oxide.

present in gypsum solutions: second, containing solutes which are electrolytes and which contain no ion in common with gypsum; and third, containing nonelectrolytes. The first class has been subdivided into two divisions, (*a*) sulphates and (*b*) calcium salts.

SOLUBILITY OF CALCIUM SULPHATE IN SULPHATE SOLUTIONS.

Ammonium sulphate:

Before any measurements were recorded on the solubility of gypsum in solutions of ammonium sulphate a double compound of these sulphates $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$ had been observed by Popp^{*a*} and by Fassbender,^{*b*} who obtained it by dissolving 285 grams of ammonium sulphate in 800 c. c. of water and saturating the solution with gypsum, and after evaporation to 500 or 600 c. c. filtering off the mother liquor at 40° to 50° C. The double salt is isomorphic with the double potassium calcium sulphate. Ditte^{*c*} obtained the double salt from a concentrated solution after allowing it to stand for some days.

Droeze^{*d*} was the first to make any determinations of the solubility of gypsum in solutions of ammonium sulphate. A saturated solution of ammonium sulphate at 8.5° to 9° C. will dissolve 3.06 grams gypsum per liter, and a solution of one-seventh saturated at 13.5° will dissolve 2.709 grams of gypsum per liter. A more complete series of determinations has been made by Cohn.^{*e*} From the diagram it will be seen that the solubility of calcium sulphate decreases with increasing amounts of ammonium sulphate in the solution, but at higher concentrations the solubility increases. The following table recalculated from Cohn's results gives the percentage of each salt compared to water at 22.5° C.

TABLE VII.—*Solubility of calcium sulphate in ammonium sulphate solutions at 22.5°.*

Parts (NH_4) ₂ SO ₄ per 100 parts solution.	Parts CaSO ₄ per 100 parts solution.	Parts (NH_4) ₂ SO ₄ per 100 parts solution.	Parts CaSO ₄ per 100 parts solution.
3.236	0.16209	18.581	0.31545
7.976	.20509	22.031	.33117
11.725	.25299	25.310	.35585
14.964	.28602	28.636	.36901

The diagram (fig. 7) shows that the solubility curve goes through a minimum, but the data are insufficient to give the concentration at this point. There seems to be no doubt that the curve is continuous, and hence no new solid phase has appeared at this temperature. It must be remembered that the double sulphate was obtained by Fassbender

^{*a*} Ann. Chem. Phar. Suppl., 8, 1 (1870-72).

^{*b*} Ber., 9, 1358 (1876); 11, 1968 (1878).

^{*c*} Compt. rend., 84, 86 (1877).

^{*d*} Ber., 10, 330 (1877).

^{*e*} Jour. prakt. Chem., 143, 43 (1887).

above 40° , and hence the double sulphate makes its appearance between 22° and the temperature at which Cohn worked.

A similar result has recently been obtained by Sullivan,^a who does not, however, refer to Cohn's work. Sullivan's experiments were conducted at 25° C., and the curve is similar to that obtained by Cohn. The solubility of gypsum at first decreases to a minimum, and then increases with increasing amounts of ammonium sulphate in the solution. At this temperature Sullivan's results indicate that the double salt does not appear. The results, which are given in mols per liter, have been changed into grams per liter; and as the densities have also been given, it is possible to calculate grams of salt per 100 grams of water, and these results have been plotted in the diagram. Sullivan's results are as follows:

TABLE VIII.—*Solubility of calcium sulphate in ammonium sulphate solutions at 25° C.*

Density at 25° .	(NH ₄) ₂ SO ₄ per 100 c. c. solution.	CaSO ₄ per 100 c. c. solution.	Density at 25° .	(NH ₄) ₂ SO ₄ per 100 c. c. solution.	CaSO ₄ per 100 c. c. solution.
	Grams.	Grams.		Grams.	Grams.
0.99911	0	0.2083	1.00341	0.8266	0.1440
.99911	.0129	.2043	1.00817	1.6532	.1455
.99920	.0258	.1996	1.01763	3.3065	.1617
.99946	.1033	.1807	1.05344	6.6130	.2330
.99995	.2067	.1658	1.10324	13.2259	.3330
1.00104	.4133	.1540	1.19149	26.4578	.4500

The solubility of gypsum has been determined by Bell and Taber^b at 50° with the following results:

TABLE IX.—*Solubility of calcium sulphate in solution of ammonium sulphate at 50° C.*

Density, 50° .	(NH ₄) ₂ SO ₄ per liter.	CaSO ₄ per liter.	Density, 50° .	(NH ₄) ₂ SO ₄ per liter.	CaSO ₄ per liter.
	Grams.	Grams.		Grams.	Grams.
.....	0	2.168	1.1968	416.0	5.345
1.0026	15.65	1.609	1.2043	428.4	4.632
1.0113	30.67	1.750	1.2187	479.4	3.524
1.0440	91.6	2.542	1.2437	540.8	2.152
1.0819	160.4	3.402	1.2480	558.0	1.986
1.1108	221.6	4.068	1.2502	564.0	1.98
1.1385	280.6	4.690	1.2508	566.0	1.08
1.1653	340.6	5.084	1.2510	566.7	0

The plot of these results shows breaks at 416 grams (NH₄)₂SO₄ per liter and at 564 grams (NH₄)₂SO₄ per liter. Between these concentrations the solid phase was a double salt of ammonium sulphate and calcium sulphate of the formula CaSO₄·(NH₄)₂SO₄·2H₂O.

Potassium sulphate.

A double salt of potassium and calcium sulphates, CaSO₄·K₂SO₄·H₂O, has been observed as a by-product in the manufacture of tartaric acid by Philips,^c Rose,^d Struve,^e Schott,^f Fassbender,^g Ditte,^h Hannay,ⁱ

^a Jour. Am. Chem. Soc., **27**, 529 (1905).

^b Jour. Phys. Chem., **10**, 119 (1906).

^c Jour. Chem. Soc., **3**, 348 (1851).

^d Ann. Phys., **93**, 1 (1854).

^e Zeit. Chem., **5**, 323 (1869).

^f Dingl. Poly. Jour., **196**, 357 (1870).

^g Ber., **9**, 1358 (1876).

^h Compt. rend., **84**, 86 (1877).

ⁱ Chem. News, **34**, 256 (1876).

Grosjean,^a and others, and it has been prepared in several different ways. Rose obtained it by mixing solutions of potassium sulphate and calcium sulphate; Struve by the action of KNO_3 , KCl , or KI solutions on gypsum solutions, although Fassbender doubts whether it can be prepared in this way from the chloride solution. The latter has also described a compound to which he gives the formula $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$, but it seems more probable that this is a mixture of the double salt and potassium chloride. The double salt has been shown to be identical with the double sulphate found together with sylvine, KCl , in Kalusz, and formerly called kaluszcite. Later, on account of this relation to polyhalite, it was called syngenite. Van 't Hoff and Wilson^b have determined the composition of the solution in equilibrium with both calcium sulphate and syngenite at 25° and have applied these data to the determination of the conditions governing the formation of syngenite.

A second double compound of the formula $2\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ and also $2\text{CaSO}_4 \cdot \text{RbSO}_4 \cdot 3\text{H}_2\text{O}$ is given by Ditte.^c The solution in equilibrium with the double salt and with solid K_2SO_4 has about the same content of K_2SO_4 per liter as the solution saturated with the double compound and gypsum. The range of concentration in equilibrium with the double salt is therefore very limited, and in contact with water the salt decomposes to the single sulphates. In a later paper Ditte^d has recorded the double sulphate $\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$. The conditions for the formation of potassium pentacalcium sulphate $\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$, which is recorded by van 't Hoff,^e are given in another place.

The only determinations of the solubility of gypsum in different potassium sulphate solutions before 1904 were by Droeze,^f who found that at 13.5°C . a saturated solution of K_2SO_4 would dissolve 0.043 gram gypsum per 100 c. c., and that a solution one-fifth saturated would dissolve 0.1505 gram gypsum per 100 c. c.

A series of determinations have been made by Cameron and Breazeale^g by adding an excess of gypsum to solutions of potassium sulphate and by adding syngenite to solutions of potassium sulphate. The following data were obtained at 25°C . The work was done in two series of experiments, series B being somewhat more carefully planned.

^a Dingl. Poly. Jour., **250**, 371 (1883).

^b Sitzungsber. Akad. Wiss. Berlin, 1900, 1142.

^c Compt. rend., **79**, 215, 956, 1254 (1874).

^d Compt. rend., **126**, 694 (1898).

^e Sitzungsber. Akad. Wiss. Berlin, 1904, 935.

^f Ber., **10**, 330 (1877).

^g Jour. Phys. Chem., **8**, 335 (1904).

TABLE X.—*Solubility of calcium sulphate in solutions of potassium sulphate at 25° C.*

Series A.			Series B.		
Weight of 1,000 c. c. of solution.	Quantity K_2SO_4 per liter.	Quantity $CaSO_4$ per liter.	Weight of 1,000 c. c. of solution.	Quantity K_2SO_4 per liter.	Quantity $CaSO_4$ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1,003.61	4.88	1.601	1,003.80	5.09	1.563
1,007.54	9.86	1.504	1,007.54	5.85	1.446
1,015.54	19.71	1.534	1,015.15	19.57	1.485
1,022.82	29.72	1.582	1,022.86	28.35	1.553
1,032.18	41.91	1.073	1,023.64	30.66	1.587
1,046.28	54.25	.551	1,024.14	31.15	1.549
1,060.35	80.04	.398	1,026.92	35.19	1.257
1,075.54	99.68	.252	1,027.32	35.79	1.213
			1,030.62	40.53	.970
			1,072.41	96.00	.257

Syngenite was prepared by dissolving 120 grams of potassium sulphate in 1,000 c. c. of water, and to this was added a solution containing 20 grams of anhydrous calcium chloride in 100 c. c. of water. After standing some time the precipitated magma was washed with 85 per cent alcohol, and finally with ordinary alcohol, until free from chlorides. This syngenite was then treated in the manner above described for the calcium sulphate in potassium sulphate solution. The concentrations of the resulting solutions in potassium sulphate and calcium sulphate are given in Table XI.

TABLE XI.—*Solubility of syngenite in solutions of potassium sulphate.*

Weight of 1,000 c. c. of solution.	Quantity K_2SO_4 per liter.	Quantity $CaSO_4$ per liter.	Weight of 1,000 c. c. of solution.	Quantity K_2SO_4 per liter.	Quantity $CaSO_4$ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Gram.</i>
1,013.08	16.31	1.495	1,036.82	46.99	0.810
1,015.78	19.87	1.529	1,058.10	75.45	.451
1,020.01	25.01	1.537	1,085.91	112.87	.330
1,024.54	30.83	1.565			

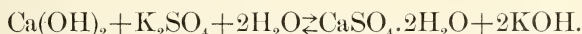
In the first four determinations the syngenite was completely decomposed, and gypsum was formed and remained as solid phase; the corresponding amounts of potassium sulphate passed into solution and increased the concentration with respect to this salt. Beyond the fourth determination the concentration with respect to potassium sulphate was sufficient for the existence of the syngenite in the solid phase.

From the accompanying diagram (fig. 7) it is evident that we are dealing here with two intersecting curves. The upper part of these two curves gives the solubility of calcium sulphate in solutions of potassium sulphate of varying concentrations, and the lower curve the solubility of the syngenite, which forms in solutions of concentrations of potassium sulphate greater than about 32 grams per liter. The first curve shows the conditions of concentration for equilibrium between potassium sulphate and calcium sulphate when the solution

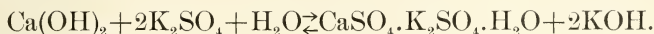
is in contact with calcium sulphate or gypsum as solid phase, and the second curve the conditions with syngenite as solid phase. The intersection of the two curves gives the stable inversion point where the solution is in equilibrium with both gypsum and syngenite as solid phases. This inversion point is somewhat lower in respect to calcium sulphate than was found by van 't Hoff and Wilson,^a who give the composition of the solution in equilibrium with the syngenite and potassium sulphate to be 30.8 grams K_2SO_4 and 1.9 grams $CaSO_4$ per liter. To test further the position of the inversion point the procedure followed by these investigators was used, and the results obtained show that the values for the inversion point at 25° C., as found by extrapolation on the curves, are substantially correct:

Procedure.	Grams per liter of solution.	
	K_2SO_4 .	$CaSO_4$.
By direct determination	32.47	1.582
By extrapolation	32.00	1.585

Potassium sulphate is employed as the source of potassium in the manufacture of caustic potash. Lime is added to solutions of potassium sulphate, and at the lower concentrations the resulting products are gypsum and caustic potash,



This reaction has been studied by Herold^b to find out the most efficient temperature and concentration for the production of alkali, and in his investigations at the lower concentration the condition has been imposed that the solution always contains solid calcium hydroxide and solid gypsum. At the higher concentrations gypsum no longer exists in equilibrium with the solutions, syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$) appearing,



Under these conditions the composition of the solutions have been found, calcium hydroxide and syngenite always being present as solids. Unfortunately the composition of the solutions were not completely determined, only the concentration of hydroxyl (OH) and of the sulphion (SO_4) having been found. No data regarding the concentration of the calcium or of potassium are recorded. The equilibrium has been approached from two directions, for calcium hydroxide has been added to solutions of potassium sulphate and gypsum has been added to solutions of caustic potash. The following table gives the concentration of the solutions, expressed in terms of millimols per liter.

^aSitzungsber. Akad. Wiss. Berlin, 1900, 1142.

^bZeit. Elektrochem., **11**, 417 (1905).

TABLE XII.—*Concentration of solutions in equilibrium with calcium hydroxide and either gypsum or syngenite.*

Temperature. °C.	Starting from K_2SO_4 .		Starting from KOH.	
	Millimols OH.	Millimols SO_4 .	Millimols OH.	Millimols SO_4 .
190	53	27	40	33
	62	69	58	70
	90	180	92	160
	94	249	94	247
	41	35	45	40
150	51	76	68	70
	82	190	91	200
	87	250	98	260
	91	320	106	320
	92		108	
70	89		96	
	40	32	42	25
	53	76	52	68
	70	215	80	210
	79	255	75-76	250
20	100	264		
	112	271		
	167	368		
	210	464		
	60	35	76?	31?
0	83	68	89	69
	103	101	116	152
	167	182	119	150
	198	248	120	150
	269	318	118	151
0	64	36	80?	27?
	85	55	92	54
	123	120	123	127
	184	162	124	124
	223	183	124	120
	278	213	120	122
	400	298		

Herold has plotted the concentration with respect to hydroxyl against the concentration with respect to sulphions and at the temperatures 0° , 20° , and 70° . The points lie on two curves, one of which represents solutions in equilibrium with both calcium hydroxide and gypsum, and the other represents solutions in equilibrium with both calcium hydroxide and syngenite. If the composition of these solutions with respect to either calcium or potassium had been determined, it would have been possible to state the best conditions for the largest yield of the desired product, potash.

Several other compounds have been recorded in the literature— $CaNH_4K(SO_4)_2H_2O$ by Fassbender,^a $K_2CaSO_4CrO_4H_2O$, $K_4CaSO_4(CrO_4)_2$, and $CaK_2Na_2(SO_4)_2CrO_4H_2O$ by Hannay.^b

Sodium sulphate.

Ditte^c states that there is no double compound of calcium and sodium sulphates even after standing for some months. The only early measurement on the solubility of gypsum by a sodium sulphate solution is by Droeze,^d who states that at 10.5° C. a saturated solution of sodium sulphate will dissolve 0.2510 gram of gypsum per 100 c.c.

^a Ber., 11, 1968 (1878).

^b Chem. News, 34, 256 (1876).

^c Compt. rend., 84, 86 (1876); 126, 694 (1898).

^d Ber., 10, 330 (1877).

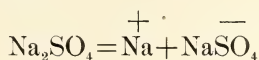
The solubility of gypsum in different sodium solutions has been studied by Cameron and Seidell.^a It was rather to be expected that the two electrolytes would yield a common sulphion, and therefore the solubility of gypsum should decrease as the concentration with respect to sodium sulphate increases. Such was found to be the case up to a concentration of about 17.5 grams per liter of sodium sulphate, when the solubility of the calcium sulphate was about 1.38 grams per liter, or of gypsum 1.745 grams per liter. At this point, as the concentration with respect to sodium sulphate increases, there is a rather sudden change in the direction of the curve and the solubility of the calcium sulphate steadily increases until, in a liter of solution containing 230 grams of sodium sulphate, there will be dissolved 2.5 grams of calcium sulphate—a quantity markedly larger than will be dissolved by pure water. The data obtained for this pair of electrolytes are given in Table XIII.

TABLE XIII.—*Solubility of calcium sulphate in solutions of sodium sulphate at 22° C.*

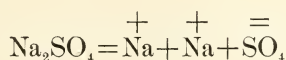
Quantity CaSO ₄ per liter.	Quantity Na ₂ SO ₄ per liter.	Quantity CaSO ₄ per liter.	Quantity Na ₂ SO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
2.084	0.000	1.841	77.320
1.583	2.771	2.185	133.000
1.433	13.820	2.414	193.800
1.408	16.360	a 2.578	a 222.580
1.569	39.310		

^a Both calcium sulphate and sodium sulphate as solid phases were in contact with the solution.

The tentative suggestion is made in this paper that possibly at concentrations with respect to sodium sulphate greater than that at the minimum point, the dissociation of the sodium sulphate takes place in part according to the scheme:



rather than entirely as indicated thus:



From this point of view one would expect the existence in the solution of a double salt, possibly of the composition $\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4$. Such a salt is the mineral glauberite found in nature. Fritzsche,^b however, describes a hydrated double sulphate ($\text{CaSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), obtained by heating gypsum with a small amount of water and a large

^aJour. Phys. Chem., **5**, 643 (1901).

^bJour. prakt. Chem., **72**, 291 (1857).

excess of Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). It was also obtained at ordinary temperatures by adding gypsum to a solution of one part sulphuric acid and two parts saturated sodium sulphate solution. The double sulphate was a well-characterized one, crystallizing in fine needles, which, on heating, quickly lost the contained water, yielding the anhydrous double salt. It was expected, therefore, that this salt, or its hydrate, might be obtained by evaporating solutions of sodium sulphate saturated with respect to calcium sulphate. Such solutions were prepared and were allowed to evaporate spontaneously at room temperature. No evidence of the presence of the double salt, however, could be detected in the residue. It should be remembered that in those areas where this double calcium sulphate has been observed in nature the ground temperatures are frequently very high, and the equilibrium condition of the solution may well be very different from those obtaining at 25°C . The anhydrous double salt has been observed also by Hannay^a and by Folkard.^b

Van 't Hoff and Chiaraviglio^c have shown that gypsum and the decahydrate of sodium sulphate will form glauberite at 25°C . if the solution be saturated with respect to both these salts and sodium chloride as well. This last substance is commonly, though perhaps not always, found in those areas from which glauberite has been reported as occurring in nature. These authors have also shown that glauberite and gypsum exist together, as solid phases, only when solid sodium sulphate (decahydrate) is not also present. The double salt is not stable in the presence of water alone, and breaks down into the simple salts, gypsum and Glauber's salt.

The following table of the solubility of gypsum in sodium sulphate solutions at 25°C . has been given in a paper published more recently by Cameron and Breazeale.^d This table shows results similar to those obtained by Cameron and Seidell^e at 22° . The concentration of the solution in equilibrium with both solid sulphates has been given by Cameron and Brown.^f In this solution there are 254.6 grams Na_2SO_4 and 2.58 grams CaSO_4 per liter at 25°C ., while at 22° the concentration as given by Cameron and Seidell^g is 222.6 grams Na_2SO_4 and 2.58 grams CaSO_4 per liter. It seems probable that at different temperatures the double salt might crystallize out, and this point ought to be investigated on account of its importance in several technical operations as well as in geological and soil studies.

^a Chem. News, **34**, 256 (1876).

^e Loc. cit.

^b Chem. News, **43**, 6 (1881).

^f Jour. Phys. Chem., **9**, 210 (1905).

^c Sitzungsber. Akad. Wiss. Berlin, 1899, 810.

^g Loc. cit.

^d Jour. Phys. Chem., **8**, 335 (1904).

TABLE XIV.—*Solubility of calcium sulphate in solutions of sodium sulphate at 25° C.*

Weight of 1,000 c. c. of solution.	Quantity Na ₂ SO ₄ per liter.	Quantity CaSO ₄ per liter.	Weight of 1,000 c. c. of solution.	Quantity Na ₂ SO ₄ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
1,001.26	2.390	1.650	1,079.47	94.220	1.980
1,007.59	9.535	1.457	1,096.47	115.084	2.096
1,011.45	14.132	1.388	1,142.66	146.612	2.234
1,020.46	24.369	1.471	1,176.47	205.105	2.503
1,031.48	36.979	1.563	1,212.00	257.100	2.650
1,039.12	46.150	1.650			

Thallium sulphate.

Ditte^a states that there is no double sulphate of calcium and thallium.

Magnesium sulphate.

The solubility of gypsum in a saturated magnesium sulphate solution is zero, according to Fassbender.^b He even proposes a method of precipitating out calcium from solutions containing large quantities of magnesium by saturating the solution with magnesium sulphate. Droeze^c also finds gypsum to be insoluble in saturated magnesium sulphate solutions, while a solution one-tenth saturated with the latter at 13.5° C. will dissolve only 0.086 gram of gypsum per 100 c. c. Ditte^a finds that magnesium sulphate forms no double compound with calcium sulphate. Cameron and Bell^d have determined this solubility at 25° C. from the loss of weight of a selenite plate in equilibrium with a known amount of a magnesium-sulphate solution of known concentration. The results are as follows:

TABLE XV.—*Solubility of calcium sulphate in magnesium sulphate solutions at 25° C.*

Density 25°	MgSO ₄ 25° per liter.	CaSO ₄ per liter.	Density 25°	MgSO ₄ 25° per liter.	CaSO ₄ per liter.	Density 25°	MgSO ₄ 25° per liter.	CaSO ₄ per liter.
	<i>Grams.</i>	<i>Grams.</i>		<i>Grams.</i>	<i>Grams.</i>		<i>Grams.</i>	<i>Grams.</i>
1.0032	0	2.046	1.0626	64.14	1.608	1.1813	198.8	1.422
1.0055	3.20	1.620	1.0833	85.67	1.617	1.2095	232.1	1.254
1.0090	6.39	1.507	1.1190	128.28	1.627	1.2382	265.6	1.070
1.0118	10.64	1.471	1.1377	149.67	1.597	1.2624	298.0	.860
1.0226	21.36	1.478	1.1479	165.7	1.549	1.2877	330.6	.647
1.0419	42.68	1.558	1.1537	171.2	1.474	1.3023	355.0	.501

^a Saturated with MgSO₄·7H₂O.

These results do not harmonize with the statements of Fassbender and Droeze, that gypsum is insoluble in saturated magnesium sulphate solution. At the temperature of 25° C. no double salt was observed.

Sulphuric acid.

One determination of the solubility of gypsum in concentrated sulphuric acid (sp. gr. = 1.82) by Struve^e gives the solubility of CaSO₄ as 2.03 parts per 100 parts of the acid. This solubility in different sulphuric acid solutions has been determined by Cameron and Brea-

^a Compt. rend., **84**, 86 (1877).

^d Jour. Phys. Chem., **10**, 210 (1906).

^b Ber., **9**, 1358 (1876).

^e Zeit. Anal. Chem., **9**, 34 (1870).

^c Ber., **10**, 330 (1877).

zeale^a for three different temperatures, 25°, 35°, and 43°, as given in Table XVI.

TABLE XVI.—*Solubility of calcium sulphate in solutions of sulphuric acid.*

Weight of 1,000 c. c. of solution at 25° C.	Quan- tity, H ₂ SO ₄ per liter.	Quantity, CaSO ₄ per liter, at—			Weight of 1,000 c. c. of solution at 25° C.	Quan- tity, H ₂ SO ₄ per liter.	Quantity, CaSO ₄ per liter, at—		
		25°.	35°.	43°.			25°.	35°.	43°.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
999.1067	0	2.126		2.145	1,043.470	75.00	2.841		4.146
1,002.493	.48	2.128	2.209	2.236	1,075.613	97.25	2.779	3.606	
1,002.553	4.87	2.144	2.451	2.456		146.01	2.571	3.150	4.139
1,005.091	8.11	2.203		2.760	1,113.392	194.70	2.313		3.551
1,009.787	16.22	2.382		3.116	1,141.755	243.35	1.901		2.959
1,030.151	48.67	2.727	3.397	3.843	1,168.143	292.02	1.541		2.481

This system presents the remarkable feature that the solubility of calcium sulphate increases with increasing amounts of sulphuric acid up to comparatively high concentrations with respect to the latter. At 25° C. the solubility of calcium sulphate is a maximum with 75 grams H₂SO₄ per liter. The solubility then decreases with stronger acid solutions.

Mixtures of potassium and magnesium sulphates.

The effect of mixtures of potassium and magnesium sulphates in solution have been studied by Basch^b under van 't Hoff's direction. In this work, the composition of solutions, saturated with a maximum number of solids, or to use van 't Hoff's term, *constant solutions*, have been determined at 25°. At this temperature the possible solid phases are gypsum, potassium sulphate, magnesium sulphate (MgSO₄·7H₂O), syngenite (K₂SO₄·CaSO₄·H₂O), schönite (MgSO₄·K₂SO₄·6H₂O), and polyhalite (K₂SO₄·2CaSO₄·MgSO₄·2H₂O). Table XVII gives the composition of the solution with respect to potassium sulphate and magnesium sulphate, the concentration of calcium being so small in most cases as to be undeterminable in the presence of large amounts of magnesium. Geiger,^c also working under van 't Hoff's direction, has studied the system composed of the same sulphates at 83°. (See Table XVII.) At this temperature the possible solid phases are anhydrite, potassium sulphate, kieserite (MgSO₄·H₂O), langbeinite (2MgSO₄·K₂SO₄), leonite (MgSO₄·(Na,K)₂SO₄·4H₂O), syngenite (K₂SO₄·CaSO₄·H₂O), pentacalcium sulphate (5CaSO₄·K₂SO₄·H₂O), polyhalite (2CaSO₄·K₂SO₄·MgSO₄·2H₂O), and krugite (4CaSO₄·K₂SO₄·MgSO₄·2H₂O). In the accompanying diagrams (figs. 5 and 6) there have been plotted the concentration in molecules of potassium sulphate and of magnesium sul-

^a Jour. Phys. Chem., **7**, 571 (1903).

^b Sitzungsber. Akad. Wiss. Berlin, 1900, 1084; Künstliche Darstellung und Bildungsverhältnisse des Polyhalits, Inaug. Diss. Berlin, 1901; also given in a paper by van 't Hoff, Zeit. anorg. Chem., **47**, 244 (1905).

^c Loc. cit.

phate per 1,000 molecules of water. The fields in the plates show the conditions of concentration under which each of the possible solid phases

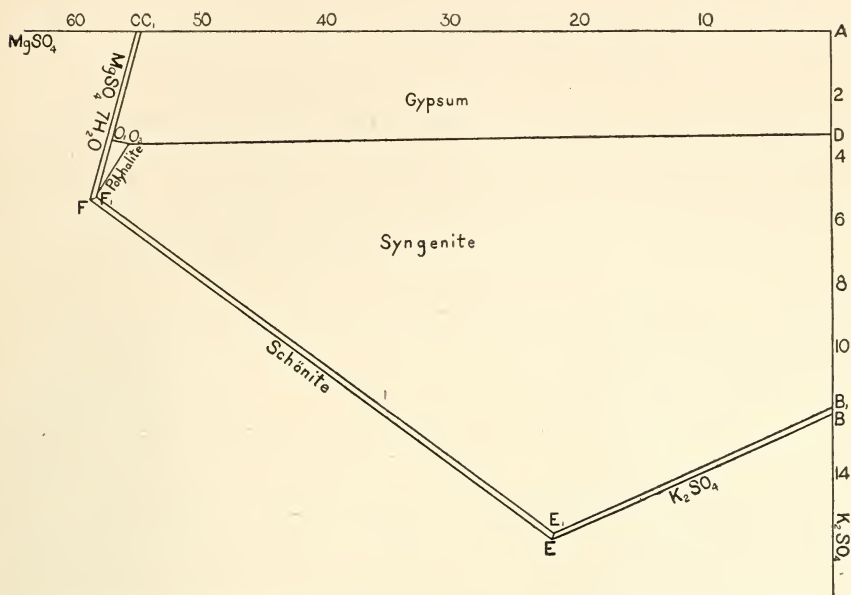


FIG. 5.—Diagram showing the conditions obtaining at 25° C. in the system composed of the sulphates of calcium, potassium, and magnesium.

may exist. For instance, it will be seen that at 25° the triple sulphate, polyhalite, exists in equilibrium with a solution within very narrow

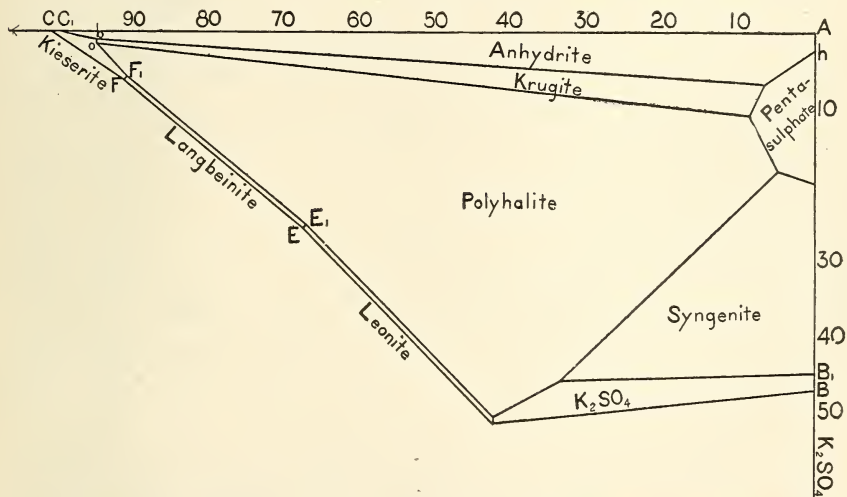


FIG. 6.—Diagram showing the conditions obtaining at 83° C. in the system composed of the sulphates of calcium, potassium, and magnesium.

limits of concentration, while the salt syngenite is the stable phase over a very much greater range of concentrations. At 83°, however,

not only have phases stable at 25° disappeared and new solid phases appeared, but also the limits of concentration, under which solids stable at both temperatures exist, have changed very greatly. Gypsum, which was the stable solid phase over a wide range of concentrations at 25° , can not exist at 83° ; krugite, pentacalcium sulphate, and anhydrite, unstable in the presence of all solutions of the three original sulphates at 25° , are stable at 83° . Syngenite, which is stable with the larger number of the possible solutions at 25° , is stable in a comparatively small number of the possible solutions at 83° , and polyhalite, which can exist at 25° with solutions within narrow limits of concentration, at 83° is the stable solid with a majority of the possible solutions.

TABLE XVII.—*Concentration of solutions, stated in mols. of salt to 1,000 mols. water, at invariant points at 25° C.*

Point on plate.	Solids present in contact with the solution.	Concentration of the solution.		
		K ₂ SO ₄ .	MgSO ₄ .	CaSO ₄ .
A	Gypsum.....	0	0	0.35
B	K ₂ SO ₄	12	0	0
C	MgSO ₄ .7H ₂ O.....	0	54.8	0
D	Gypsum, syngenite.....	3.3	0	.25
E	K ₂ SO ₄ , schönite.....	16	22	0
F	MgSO ₄ .7H ₂ O, schönite.....	5.3	58.3	0
B ₁	K ₂ SO ₄ , syngenite.....	12	0	
C ₁	MgSO ₄ .7H ₂ O, gypsum.....	0	54.8	
E ₁	K ₂ SO ₄ , schönite, syngenite.....	16	22	
F ₁	MgSO ₄ .7H ₂ O, schönite, syngenite.....	5.3	58.3	
O ₁	Polyhalite, MgSO ₄ .7H ₂ O, gypsum.....	3.6	55.7	
O ₂	Polyhalite, syngenite, gypsum.....	3.5	56.7	
O ₃	Polyhalite, MgSO ₄ .7H ₂ O, syngenite.....	5.1	58.1	

TABLE XVIII.—*Concentration of solutions, stated in mols. of salt to 1,000 mols. water at invariant points at 83° .*

Point on plate.	Solids present in contact with the solution.	Concentration of the solution.	
		K ₂ SO ₄ .	MgSO ₄ .
A	Anhydrite.....	0	0
B	K ₂ SO ₄	45.5	0
C	Kieserite.....	0	100.5
D	K ₂ SO ₄ , leonite.....	51	42.5
E	Langbeinite, leonite.....	25.5	67
F	Langbeinite, kieserite.....	6	90.5
B	K ₂ SO ₄ , syngenite.....	45	0
C ₁	Kieserite, anhydrite.....	0	100.5
D ₁	K ₂ SO ₄ , leonite, polyhalite.....	51	42.5
E ₁	Leonite, langbeinite, polyhalite.....	25.5	67
F ₁	Langbeinite, kieserite, polyhalite.....	6	90.5
G	K ₂ SO ₄ , syngenite, polyhalite.....	46	33.5
b	Kieserite, anhydrite, krugite.....	1	94
h	Pentasulphate, anhydrite.....	2.5	0
n	Pentasulphate, anhydrite, krugite.....	7	6.5
o	Kieserite, polyhalite, krugite.....	(1)	(94)
p	Pentasulphate, polyhalite, krugite.....	11	8.5
q	Syngenite, pentasulphate, polyhalite.....	18.5	4.5
r	Syngenite, pentasulphate.....	20	0

The line AC₁ of figure 5 represents solutions which contain magnesium and calcium sulphates and which are saturated with gypsum. The composition of these solutions with respect to calcium sulphate has been determined in this laboratory.^a

^a Cameron and Bell, Jour. Phys. Chem., 10, 210 (1906).

The line CC_1 represents solutions which contain the same components as before, but which are saturated with magnesium sulphate ($MgSO_4 \cdot 7H_2O$). At the point C_1 , representing a "constant solution," the solids are gypsum and magnesium sulphate. The data for the concentration of the solution as found by Basch agrees well with the data determined in this laboratory.^a

The line AB represents solutions which contain potassium sulphate and calcium sulphate. The part of the line AD represents solutions saturated with gypsum, and at D there is a complete change in the solid phase, a double sulphate of calcium and potassium (syngenite) appearing and gypsum disappearing. At D we have therefore solutions saturated with respect to both gypsum and syngenite, the length of the line AD representing the concentration of potassium sulphate in the solution at this point. The content of calcium sulphate in the solutions along AB have been determined by Cameron and Breazeale,^b and the composition of the solution at the point D , a "constant" solution, as found by Basch agrees fairly well with the data of Cameron and Breazeale.

At points within the diagram there are solutions containing all three sulphates, the solid phase being that indicated on the diagram. There are five "constant solutions," at O_1 , O_2 , O_3 , F_1 , and E_1 . At O_2 , for instance, the solution is saturated with gypsum, syngenite, and polyhalite, the fields all meeting in that point. Similarly, at the points representing the other constant solutions the solid phases are those whose fields meet in that point.

The line AC represents solutions containing no potassium sulphate, and the line AB represents solutions containing no magnesium sulphate. Using this method of representation the solutions containing no calcium sulphate are represented by the line CF , along which $MgSO_4 \cdot 7H_2O$ is the stable solid, the line FE , along which schönite is the stable solid, and the line EB , along which potassium sulphate is the stable solid.

General remarks on the effect of sulphates.

The results of all these investigations have been recalculated where it has been necessary to plot them on the same scale.

It will be observed from this diagram (fig. 7) that all the sulphates, with the exception of sulphuric acid, decrease the solubility of gypsum, as would be expected of compounds with a common ion. In the case of sulphuric acid solution containing 0.48 gram per liter the solubility of gypsum is the same as in pure water, and it seems probable that there may be a slight falling off in solubility for lower concentrations of sulphuric acid. At the higher concentrations in all cases the solu-

^aCameron and Bell, Jour. Phys. Chem., **10**, 210 (1906).

^bJour. Phys. Chem., **8**, 334 (1904).

bility increases, indicating that there is certainly some factor or factors other than the common ion influencing the solubility. It is sug-

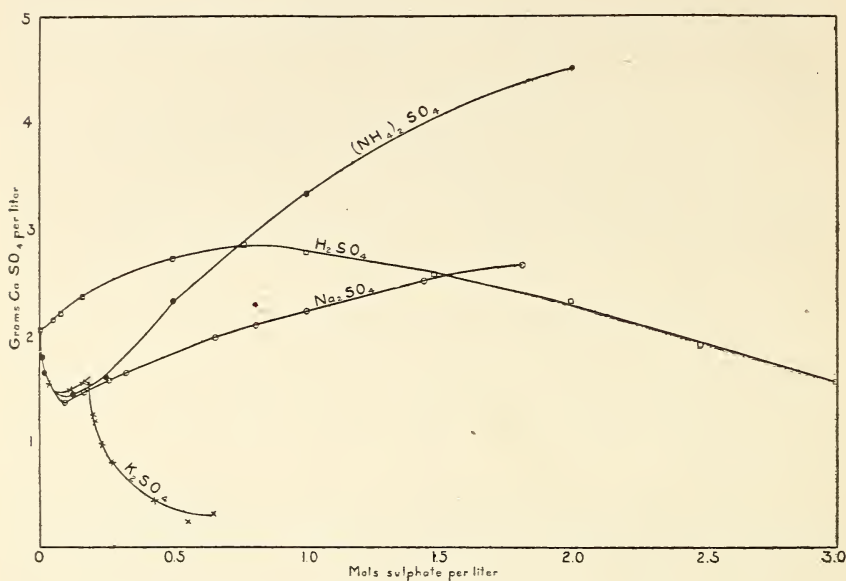
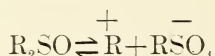
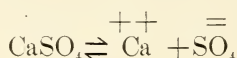


FIG. 7.—Solubility of calcium sulphates in various sulphate solutions at 25° C.

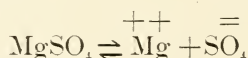
gested that at higher concentrations the sulphates of the type R_2SO_4 dissociated according to the scheme



and as the ions are different from those of calcium sulphate, which can hardly dissociate according to any other scheme than



then the solubility will tend to increase. However, in the case of magnesium sulphate, which dissociates similarly to calcium sulphate,



there is certainly a common ion added, yet we have the same kind of an increasing solubility. It seems fair to suppose, therefore, that there is some other factor of which as yet we are completely ignorant. This solubility curve in the case of magnesium sulphate and of sulphuric acid shows a maximum point; in the case of sodium, potassium, and ammonium sulphate the curvature indicates an approach to a maximum point, but before it is reached the curve ends, for a new phase

appears. It seems reasonable to suppose that for small amounts of the salt the solubility of gypsum is depressed by the addition of a common ion, but at greater concentrations some specific solvent action of the undissociated salt or of the ions themselves is experienced and the curve rises, or else the dissociation of the dissolved salts may be partial, thus giving no common ion. The assumption of any specific solvent action seems also to be rather doubtful, for at high concentrations the curves seem to pass through a maximum and decrease again. Another possible factor influencing the solubility of one salt in the solutions of another salt is the change in density of water consequent upon the addition of the salt. An appreciable change in the density of water can be brought about, at constant temperature, only by an enormous pressure, which would be so great as to materially alter the solubility of a second salt.

It is apparent that all the factors governing the solubility are not yet unknown, and no consistent formulation can be made with our present data.

SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF CALCIUM SALTS.

Calcium hydroxide.

The mutual solubility of gypsum in lime solutions and of calcium hydroxide in gypsum solutions has quite recently been determined at 25° C. in this laboratory by Cameron and Bell with the following results:

TABLE XIX.—*Mutual solubility of gypsum and lime at 25° C.*

CaSO ₄ per liter.	CaO per liter.	Solid phase.
<i>Grams.</i>	<i>Grams.</i>	
0	1.166	Ca(OH) ₂ .
.391	1.141	Ca(OH) ₂ .
.666	1.150	Ca(OH) ₂ .
.955	1.215	Ca(OH) ₂ .
1.214	1.242	Ca(OH) ₂ .
1.588	1.222	Ca(OH) ₂ , CaSO ₄ .2H ₂ O.
1.634	.939	CaSO ₄ .2H ₂ O.
1.722	.611	CaSO ₄ .2H ₂ O.
1.853	.349	CaSO ₄ .2H ₂ O.
1.918	.176	CaSO ₄ .2H ₂ O.
2.032	.062	CaSO ₄ .2H ₂ O.
2.126	0	CaSO ₄ .2H ₂ O.

It will be seen from these results that with increasing lime content in the solution the solubility of gypsum is steadily depressed. With increasing amounts of gypsum in the solution the solubility of lime seems to be nearly the same as in pure water.

Calcium chloride.

Tilden and Shenstone^a have determined at different temperatures the solubility of calcium sulphate in solutions containing 15 parts of

^a Proc. Roy. Soc., 38, 331 (1885).

calcium chloride to 100 parts of water. They find a maximum solubility in the neighborhood of 95° C. The data are as follows, the determinations at high temperatures being made, of course, in sealed tubes:

TABLE XX.—*Solubility of calcium sulphate in solutions of calcium chloride.*

Temperature.	Parts CaCl_2 per 100 parts H_2O .	Quantity CaSO_4 in 100 c. c. solution.	Temperature.	Parts CaCl_2 per 100 parts H_2O .	Quantity CaSO_4 in 100 c. c. solution.
$^{\circ}\text{C}$.		Gram.	$^{\circ}\text{C}$.		Gram.
15	15.00	0.063	94	15.16	0.110
21	14.70	.086	138	14.70	.070
39	15.00	.091	170	14.82	.081
72	14.90	.100	195	14.70	.022

These results show that there is a break in the curve at about 100° , which has been found by van 't Hoff and Armstrong^a to be the point at which there is a change of solid phase.

Lunge^b has determined the solubility of gypsum in different calcium chloride solutions at 23 – 25° C. and at 101 – 103° C., with the following results:

TABLE XXI.—*Solubility of calcium sulphate in solutions of calcium chloride.*

Temperature.	Per cent CaCl_2 solution.	Quantity CaSO_4 in 100 c. c. of solution.	Temperature.	Per cent CaCl_2 solution.	Quantity CaSO_4 in 100 c. c. of solution.
$^{\circ}\text{C}$.		Gram.	$^{\circ}\text{C}$.		Gram.
23	3.54	0.1225	25.0	16.91	0.0702
24	6.94	.0963	101.0	3.54	.1370
25	10.35	.0886	102.5	10.36	.1426
25	15.90	.0734	103.5	16.91	.1301

The solubility at 25° has been given by Cameron and Seidell^c as follows:

TABLE XXII.—*Solubility of calcium sulphate in solutions of calcium chloride at 25° C.*

Quantity CaSO_4 per liter.	Quantity CaCl_2 per liter.	Quantity CaSO_4 per liter.	Quantity CaCl_2 per liter.
Grams.	Grams.	Grams.	Grams.
2.056	0.000	1.016	51.530
1.244	7.489	.841	97.023
1.181	11.959	.465	192.705
1.096	25.770	.203	280.303
1.080	32.045	.032	367.850

^aSitzungsber. Akad. Wiss. Berlin, 1900, 559.

^bJour. Soc. Chem. Ind., 4, 31 (1885).

^cJour. Phys. Chem. 5, 643 (1901).

The solubility of gypsum in calcium chloride solutions as given by Orloff^a is as follows:

TABLE XXIII.—*Solubility of calcium sulphate in solutions of calcium chloride.*

Proportion CaCl ₂ in solution.	Quantity of CaSO ₄ in 100 grams of solution.	Proportion CaCl ₂ in solution.	Quantity of CaSO ₄ in 100 grams of solution.
<i>Per cent.</i>	<i>Grams.</i>	<i>Per cent.</i>	<i>Gram.</i>
0.5	1.4040	15.0	0.7614
1.0	1.1300	20.0	.5548
2.0	1.125	30.0	.1868
5.0	1.0362	40.0	.1278
10.0	.8513		

The solubility of the calcium sulphate decreases very rapidly as the concentration with respect to calcium chloride increases, until a concentration of about 20 grams per liter of this latter salt is reached. From this point the solubility of the calcium decreases more slowly, but steadily, and by extrapolation on the curve it would seem that a solution containing 375 grams per-liter of calcium chloride would dissolve practically no calcium sulphate.

Just why there should be so marked a change in the solubility of the calcium sulphate in solution concentrations of about 2 per cent calcium chloride does not admit of explanation as yet. It is possible that at concentrations above this the calcium chloride may partially dissociate in such a way as to form complex ions containing both calcium and chlorine,^b and thus diminish the proportional effect of calcium as ions in the solutions, forcing back the dissociation of the calcium chloride and consequently the retarding effect upon the solubility of the calcium sulphate. It seems probable, however, that the density of the solvent itself may have an important rôle in this connection.

The effect of calcium chloride in solution upon the transition temperature of gypsum has been determined by van 't Hoff and Armstrong by consideration of the vapor pressures of the solid gypsum and of that of the solution in question. For a saturated solution this temperature is about 17°; for a 15 per cent solution it is slightly over 100° C. This temperature agrees with the results of Tilden and Shennstone^c on the solubility of calcium sulphate in solutions of calcium sulphate.

Calcium nitrate.

The effect of calcium nitrate in solution upon the solubility of calcium sulphate at 25° has been studied by Seidell and Smith.^d The results of this work are given in Table XXIV.

^a Jour. Russ. Phys. Chem. Soc., **34**, 949 (1902).

^b Noyes. Phys. Rev., **12**, 15 (1901); Jour. Am. Chem. Soc., **23**, 37 (1901); Zeit. phys. Chem., **36**, 61 (1901).

^c Proc. Roy. Soc., **38**, 331 (1885).

^d Jour. Phys. Chem., **8**, 493 (1904).

TABLE XXIV.—*Solubility of calcium sulphate in solutions of calcium nitrate at 25° C.*

Weight of 1,000 c. c. of solution.	Quantity $\text{Ca}(\text{NO}_3)_2$ per liter of solution.	Quantity CaSO_4 per liter of solution.	Weight of 1,000 c. c. of solution.	Quantity $\text{Ca}(\text{NO}_3)_2$ per liter of solution.	Quantity CaSO_4 per liter of solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
998.1	0	2.084	1,203.5	300	0.759
1,013.8	25	1.238	1,265.6	400	.569
1,031.7	50	1.196	1,328.1	500	.403
1,067.3	100	1.134	1,352	544	.346
1,136.9	200	.929			

General remarks on the effect of calcium salts.

The effect of calcium salts on the solubility of calcium sulphate is to depress the solubility more and more as the amount of the calcium salt increases. This result is in no way remarkable, as it follows the rule that the addition of a salt with a common ion depresses the solubility.

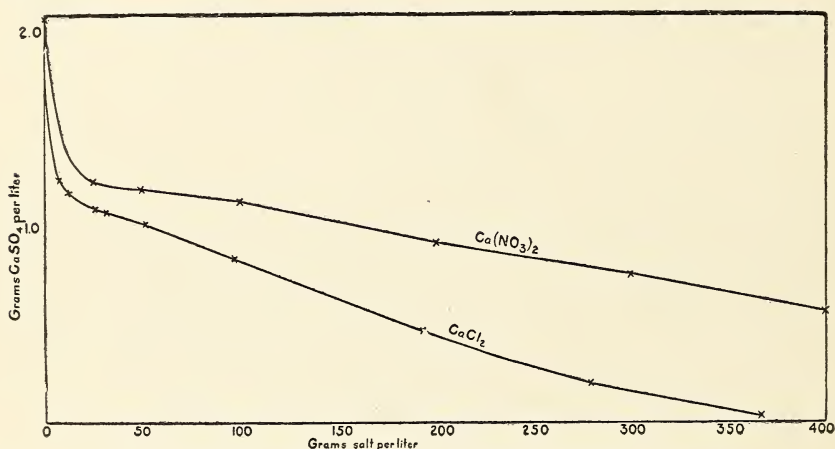


FIG. 8.—Solubility of calcium sulphate in solutions of calcium salts at 25° C.

SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF ELECTROLYTES NOT CONTAINING A COMMON ION.

Hydrochloric acid.

The solubility of calcium sulphate in hydrochloric acid solutions has been studied by Banthisch,^a working under Oswald's direction, and the results of this investigation have been recalculated so as to give grams of each solute per liter of solution.

TABLE XXV.—*Solubility of calcium sulphate in hydrochloric acid solutions at 25° C.*

Quantity HCl per liter of solution.	Quantity CaSO_4 per liter of solution.
<i>Grams.</i>	<i>Grams.</i>
0	(2.062)
3.618	4.357
18.090	9.935
36.180	13.565
72.360	17.275

^aJour. prakt. Chem., 137, 52 (1884).

Lunge's results^a on this subject can not be calculated on the same basis, but, assuming the density of the solution to be the same as water (and they do not vary much from this figure), it will be seen from Table XXV that they agree well with Banthisch's results at 25°.

TABLE XXVI.—*Solubility of calcium sulphate in hydrochloric acid solutions at 25° C.*

Temperature.	Proportion of HCl.	Quantity CaSO ₄ per liter of solution.	Temperature.	Proportion of HCl.	Quantity CaSO ₄ per liter of solution.
° C.	Per cent.	Grams.	° C.	Per cent.	Grams.
25	0.77	6.405	25	6.12	16.539
25	1.56	8.821	101	.77	11.209
25	3.06	12.639	102	3.06	31.780
25	4.70	15.342	103	6.12	46.902

Ammonium chloride.

The solubility of gypsum has been found by Vogel^b to be greater in ammonium chloride than in pure water.

Fassbender^c gives the ratio of gypsum to ammonium chloride as 1 to 92 in a saturated solution at 15°. The following results have been determined by Droeze:^d

TABLE XXVII.—*Solubility of calcium sulphate in ammonium chloride solutions.*

Temperature.	Concentration of NH ₄ Cl solution.	Quantity CaSO ₄ per liter of solution.
° C.		Grams.
13.5.....	Saturated	10.772
13.5.....	1 part saturated	10.320
13.5.....	2 parts saturated	4.988
Boiling..	10 parts saturated	5.461

Tilden and Shenstone^e have studied the effect of temperature on the solubility of CaSO₄ in a solution of ammonium chloride containing 25 parts of the salt to 100 parts of water. The results in Table XXVIII show a maximum solubility in the neighborhood of 60°.

TABLE XXVIII.—*Solubility of calcium sulphate in 20 per cent solutions of ammonium chloride.*

Temperature.	Quantity CaSO ₄ in 100 grams water.	Temperature.	Quantity CaSO ₄ in 100 grams water.
° C.	Grams.	° C.	Grams.
8	1.030	60	1.133
9	1.023	80	1.026
25	1.096	120	1.000
39	1.126		

^aJour. Soc. Chem. Ind., 4, 31 (1885).

^dBer., 10, 330 (1877).

^bRept. Phar. (3), 5, 342 (1850).

^eProc. Roy. Soc., 33, 331 (1885).

^cBer., 9, 1358 (1876).

Table XXIX gives Cohn's results^a recalculated to give the amount of each salt in 100 grams of water.

TABLE XXIX.—*Solubility of calcium sulphate in ammonium chloride solutions at 20° C.*

Quantity of NH_4Cl in 100 parts solution.	Quantity CaSO_4 in 100 parts solution.	Quantity of NH_4Cl in 100 parts solution.	Quantity CaSO_4 in 100 parts solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
3.242	0.56391	16.105	0.83311
6.617	.71065	18.730	.81276
10.488	.79769	21.360	.78219
12.036	.82522	25.327	.74354

These results show either that the solubility has become practically constant at higher concentrations or that it has reached a maximum point and tends to fall off again.

The results obtained by Ditte^b show no such maximum, when recalculated to give grams of each salt per liter of solution.

TABLE XXX.—*Solubility of calcium sulphate in solutions of ammonium chloride.*

Quantity NH_4Cl per liter of solution.	Quantity CaSO_4 per liter of solution.	Quantity NH_4Cl per liter of solution.	Quantity CaSO_4 per liter of solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
0	2.43	120	9.13
20	5.38	200	9.71
40	6.94	280	10.25
60	8.01	353	10.69
80	8.91		

The data published by Cameron and Brown,^c however, show a distinct maximum point at 25°.

TABLE XXXI.—*Solubility of calcium sulphate in ammonium chloride solution at 25°.*

Quantity NH_4Cl per liter of solution.	Quantity CaSO_4 per liter of solution.	Quantity NH_4Cl per liter of solution.	Quantity CaSO_4 per liter of solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
10.8	3.90	195.6	10.85
24.4	5.38	210	10.88
46.7	7.07	275	10.60
94.5	8.80	325	9.40
149.7	10.30	a 376.3	7.38

^a Saturated.

Sodium Chloride.

The earliest experimenter on the solubility of gypsum in common salt solutions was Droeze^d. His results, given in the following table, can not be computed for comparison with any of the latter work.

^a Jour. prakt. Chem., **143**, 43 (1887).

^c Jour. Phys. Chem., **9**, 210 (1905).

^b Compt. rend., **126**, 694 (1898).

^d Ber., **10**, 330 (1877).

TABLE XXXII.—*Solubility of calcium sulphate in solutions of sodium chloride.*

Tempera- ture.	Concentration of NaCl solution.	Quantity gypsum in 100 c. c.
° C.		Gram.
8.5	saturated	0.6785
13.5	do	.6665
13.5	saturated	.6708
13.5	saturated	.1085

Tilden and Shenstone^a have studied the effect of temperature upon the solubility of gypsum in salt solutions containing 20 parts of salt to 100 parts of water. Their results are given in Table XXXIII.

TABLE XXXIII.—*Solubility of calcium sulphate in solutions of sodium chloride.*

Tempera- ture.	Parts NaCl to 100 parts H ₂ O.	Part CaSO ₄ to 100 parts H ₂ O.	Tempera- ture.	Parts NaCl to 100 parts H ₂ O.	Part CaSO ₄ to 100 parts H ₂ O.
° C.			° C.		
20	19.90	0.823	130	19.92	0.392
44	19.93	.830	165	20.04	.250
67	19.95	.832	169	20.05	.244
85	19.90	.823	179	20.10	.229
101	20.08	.682	225	21.00	.178

It will be seen from the table that the solubility drops abruptly at about 100° C. There is a change of solid phase in this neighborhood, CaSO₄·2H₂O changing into 2CaSO₄·H₂O at 95°, as has been shown by van 't Hoff and Armstrong.^b Tilden and Shenstone have also determined the solubility of calcium sulphate in different salt solutions at 20° C., with the results shown in Table XXXIV.

TABLE XXXIV.—*Solubility of calcium sulphate in solutions of sodium chloride at 20° C.*

Parts NaCl to 100 parts water.	Part CaSO ₄ to 100 parts water.	Parts NaCl to 100 parts water.	Part CaSO ₄ to 100 parts water.
0.000	0.225	10.00	0.738
.52	.301	20.00	.823
2.03	.441	24.40	.820
5.02	.615	35.10	.734
5.05	.634	35.86	.709

These figures show that there is a maximum solubility at 20° in a solution of salt containing 20 parts of salt to 100 parts of water.

The results of Lunge^c indicate that the solubility of gypsum increases with the amount of common salt in the solution, and also that for the same solution the solubility is lower at 100° than at 20° C.

^aProc. Roy. Soc., **38**, 331 (1885).

^bSitzungsber. Akad. Wiss. Berlin, 1900, 559.

^cJour. Soc. Chem. Ind., **4**, 31 (1885).

TABLE XXXV.—*Solubility of calcium sulphate in sodium chloride solutions.*

Temperature.	NaCl in solution.	CaSO ₄ per 100 c. c. of solution.	Temperature.	NaCl in solution.	CaSO ₄ per 100 c. c. of solution.
° C.	Per cent.	Gram.	° C.	Per cent.	Gram.
21.5	3.53	0.5715	17.0	17.46	0.7369
19.5	7.35	.6429	101.0	3.53	.4891
21.0	11.12	.7215	102.5	14.18	.6248
18.0	14.18	.7340	103.0	17.46	.6299

Ditte^a finds that at the temperature at which he worked (about room temperature) there is no separation of a double sulphate of calcium and sodium. Cameron^b has determined the solubility of calcium sulphate in different sodium chloride solutions at several temperatures. In Tables XXXVI and XXXVII are the results of this work:

TABLE XXXVI.—*Solubility of calcium sulphate in sodium chloride solutions at different temperatures.*

[Grams per liter.]

At 15° C.		At 23° C.		At 26° C.		
NaCl.	CaSO ₄ .	NaCl.	CaSO ₄ .	NaCl.	CaSO ₄ .	Density of solution.
0.6	2.3	0.99	2.37	0	2.121	0.9998
1.1	2.5	4.95	3.02	91.154	6.656	1.0644
5.1	3.1	10.40	3.54	143.989	7.179	1.0981
10.6	3.7	30.19	4.97	148.343	7.164	1.1012
31.1	4.8	49.17	5.94	176.502	7.119	1.1196
51.4	5.6	75.58	6.74	228.756	6.791	1.1488
139.9	7.4	129.50	7.50	264.173	6.498	1.1707
		197.20	7.25	320.491	5.715	1.2034
		229.70	7.03			
		306.40	5.68			
		^a 315.55	5.37			

^a Saturated.TABLE XXXVII.—*Solubility of calcium sulphate in sodium chloride solutions at different temperatures.*

[Grams per liter.]

At 30° C.		At 52° C.		At 70° C.		At 82° C.	
NaCl.	CaSO ₄ .	NaCl.	CaSO ₄ .	NaCl.	CaSO ₄ .	NaCl.	CaSO ₄ .
0.5	2.5	0.5	2.3	0.5	2.2	0	2.07
10.3	3.6	1.1	2.4	10.0	3.4	1.0	2.18
30.3	5.0	5.0	2.9	29.6	4.9	5.0	2.65
47.3	6.1	10.1	3.5	48.8	5.8	10.1	3.30
73.4	6.9	29.6	5.0	132.7	7.4	29.5	4.68
126.9	7.3	48.3	5.8	195.0	7.6	48.8	5.54
192.4	7.7	75.7	6.6			74.9	6.23
		131.6	7.1			128.7	7.00
		195.6	7.4			195.1	7.51

It is to be seen from these observations, at least at the lower temperatures, 23° and 26°, that the result of Tilden and Shenstone is confirmed, namely, that there is a maximum in the solubility curve. This does not seem to exist for temperatures above 30°.

^a Compt. rend., 126, 694 (1898).^b Jour. Phys. Chem., 5, 556 (1901).

The following results by Orloff^a indicate that there is a maximum in the solubility curve.

TABLE XXXVIII.—*Solubility of calcium sulphate in solutions of sodium chloride.*

NaCl in solution.	Quantity of CaSO ₄ in 100 grams solution.	NaCl in solution.	Quantity of CaSO ₄ in 100 grams solution.
<i>Per cent.</i>	<i>Grams.</i>	<i>Per cent.</i>	<i>Grams.</i>
0.5	2.8885	10.0	6.5385
1.0	3.3652	15.0	6.4222
2.0	4.2602	20.0	5.8991
5.0	5.5737		

The results of Cloez^b do not agree well with the above results by Orloff and by Cameron, for no maximum solubility is found. The results at 14° C. are as follows:

TABLE XXXIX.—*Solubility of calcium sulphate in sodium chloride solutions at 14° C.*

Concentration of NaCl in 100 c. c. of solution.	Quantity of CaSO ₄ in 100 c. c. of solution.	Concentration of NaCl in 100 c. c. of solution.	Quantity of CaSO ₄ in 100 c. c. of solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
2.44	0.635	14.22	0.193
4.77	.826	23.12	1.275
9.50	1.056	31.30	1.583

The solubility of gypsum in common salt solutions has been determined by d'Anselme^c who found that brines from salt wells always contain more gypsum than the same amount of pure water would dissolve. This content of gypsum always causes trouble in the preparation of soda from the salt, for in the ammonia process the mixed gases carbon dioxide and ammonia always precipitate the lime from solution. These solubility determinations are in very good accord with those of Cameron.

TABLE XL.—*Solubility of calcium sulphate in sodium chloride solutions at different temperatures.*

[Grams per liter.]

NaCl.	CaSO ₄ at 14° C.	CaSO ₄ at 20° C.	NaCl.	CaSO ₄ at 14° C.	CaSO ₄ at 20° C.	NaCl.	CaSO ₄ at 14° C.	CaSO ₄ at 20° C.
0	1.70	2.10	58.50	5.72	6.00	160.8	7.00	7.05
2.925	2.32	2.70	87.75	6.58	6.85	175.6	6.80	6.89
5.850	2.79	3.15	102.3	6.90	7.15	204.7	6.30	6.30
11.70	3.41	3.75	117.0	7.10	7.30	234.0	5.90	5.90
14.62	3.68	4.00	131.6	7.20	7.30	263.2	5.50	5.52
29.25	4.40	4.70	146.2	7.10	7.13	292.6	5.30	5.30

^aJour. Russ. Phys. Chem. Soc., **34**, 949 (1902).

^bBul. Soc. Chim. (3), **29**, 167 (1903).

^cBul. Soc. Chim. (3), **29**, 372 (1903).

The effect of sodium chloride in solution upon the transition temperature of gypsum has been studied by van 't Hoff and Armstrong^a by the method of vapor tensions. The vapor tension curve for gypsum crosses the vapor tension curve of the solution saturated with both salts at the temperature 77° C., and consequently this is the transition temperature of gypsum in the presence of a solution saturated with common salt. For a 17 per cent salt solution this temperature was found to be at 95°, a result which is in accord with the experimental results of Tilden and Shenstone^b on the solubility of calcium sulphate in a 17 per cent salt solution. The solubility curve abruptly changes its direction at about this temperature, owing to the change in the stable solid phase. For a 3½ per cent solution the transition temperature was found to be 105° C.

Potassium chloride.

Comparatively little work has been done on the solubility of calcium sulphate in potassium chloride solution. Fassbender^c gives the result of one experiment; at 8° C. 1 part of gypsum dissolves in 162 parts of saturated potassium chloride solution. Droeze^d confirms the result and finds that 1 part of gypsum dissolves in 295 parts of a one-fifth saturated KCl solution. The solubility of gypsum in different KCl solutions at 21° has been studied by Ditte.^e His results indicate that at high concentrations the double sulphate crystallizes out, leaving less of the SO₄ group in solution than corresponds to the calcium in solution. The results have been recalculated, and are given in Table XLI.

TABLE XLI.—*Solubility of calcium sulphate in potassium chloride solutions at 21° C.*

Quantity KCl per liter.	Quantity CaSO ₄ per liter.	Quantity KCl per liter.	Quantity CaSO ₄ per liter.
Grams.	Grams.	Grams.	Grams.
0	2.05	24	3.75
4	2.32	40	4.73
12	3.06	60	5.28
20	3.61	80	5.84

For greater concentrations the solid phase was not gypsum, but the double sulphate.

Potassium bromide and potassium iodide.

Ditte^f says the results for these two salts are similar to those for the chloride, i. e., the solubility increases with increasing salt content until the double sulphate separates.

^a Sitzungsber. Akad. Wiss. Berlin, 1900, 559.

^b Proc. Roy. Soc., 38, 331 (1885).

^c Ber., 9, 1358 (1876).

^d Ber., 10, 330 (1877).

^e Compt. rend., 126, 694 (1898).

^f Compt. rend., 126, 694 (1898); see also Struve, Zeit. Chem., 5, 324 (1869).

Magnesium chloride.

One result on the solubility of gypsum is given by Droeze,^a namely, 1 part of gypsum dissolves in 146 parts of a one-ninth saturated MgCl_2 solution at 13.5°C . Tilden and Shenstone^b have given determinations at three temperatures (see Table XLII) on which no conclusion can be based.

TABLE XLII.—*Solubility of calcium sulphate in solutions of magnesium chloride.*

Temperature.	Quantity of salt in 100 parts water.	
	MgCl_2 .	CaSO_4 .
	Grams.	Grams.
9	19.8	0.771
39	11.1	2.774
80	9.99	1.038

Cameron and Seidell^c have studied the solubility of calcium sulphate in magnesium chloride solutions at 26° . The results of their work are given in Table XLIII.

TABLE XLIII.—*Solubility of calcium sulphate in solutions of magnesium chloride at 26°C .*

[Grams per liter.]

Water.	MgCl_2 .	CaSO_4 .	Water.	MgCl_2 .	CaSO_4 .
997.924	0	2.082	972.218	121.381	8.622
996.520	8.501	4.258	949.950	206.985	6.567
994.489	19.175	5.692	908.678	336.986	2.774
989.143	46.640	7.588	878.588	441.128	1.385

It is evident from the table that the solubility of CaSO_4 passes through a maximum. The content of CaSO_4 in 100 grams of a 10 per cent solution of MgCl_2 is given by Orloff^d as 8.966 grams. The solution saturated with both salts at 25° contains^e 476.9 grams MgCl_2 per liter and 1.09 grams CaSO_4 per liter.

The transition temperature for gypsum in the presence of a solution saturated with magnesium chloride has been determined by van 't Hoff and Armstrong^f to be about 11°C .

Nitric acid.

The measurements of Banthisch^g on the solubility of gypsum in nitric acid solutions shows that the amount of gypsum in solution

^a Ber., **10**, 340 (1877).^b Proc. Roy. Soc., **38**, 331 (1885).^c Jour. Phys. Chem., **5**, 643 (1901).^d Jour. Russ. Phys. Chem. Soc., **34**, 949 (1902).^e Cameron and Brown, Jour. Phys. Chem., **9**, 210 (1905).^f Sitzungsber. Akad. Wiss. Berlin, 1900, 559.^g Jour. prakt. Chem., **137**, 52 (1884).

increases with increasing concentration of the acid. These results are as follows:

TABLE XLIV.—*Solubility of calcium sulphate in solutions of nitric acid at 25° C.*

Quantity HNO ₃ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>
6.257	4.397
31.285	10.435
62.57	15.147
225.14	20.607

Ammonium nitrate.

Droeze^a has studied the solubility of gypsum in ammonium nitrate solutions and has found that at 13.5° the solubility passes through a maximum point, as the following table shows. The results can not be computed for comparison with more modern data.

TABLE XLV.—*Solubility of calcium sulphate in ammonium nitrate solutions at different temperatures.*

Temper- ature.	Concentration of NH ₄ NO ₃ solution.	Quantity of gypsum in 100 c.c.
° C.		<i>Grams.</i>
8-9	Saturated.....	0.312
13.5	$\frac{3}{4}$ saturated.....	1.843
13.5	$\frac{2}{7}$ saturated.....	.967

The results of Cohn^b have been recalculated to give the percentage amount of each salt in the solution.

TABLE XLVI.—*Solubility of calcium sulphate in ammonium nitrate solutions at different temperatures.*

At 20° C.		At 27.5° C.	
Quantity NH ₄ NO ₃ per 100 grams solution.	Quantity CaSO ₄ per 100 grams solution.	Quantity NH ₄ NO ₃ per 100 grams solution.	Quantity CaSO ₄ per 100 grams solution.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
4.667	0.6074	27.544	1.0250
8.490	.7720	35.932	1.0190
14.346	.9006	43.616	.9680
18.883	.9701	51.148	.8845
23.229	1.0220	58.503	.7965
28.211	1.0480	63.814	.7227
30.905	1.0467		
36.089	1.0308		

From the first two columns of the above table it will be observed that the solubility reaches a maximum at about 29 per cent NH₄NO₃ at 20° C. The results in the second two columns of this table describe solutions quite concentrated with ammonium nitrate, when the solubility has apparently passed through the maximum.

^a Ber., 10, 330 (1877).

^b Jour. prakt. Chem., 143, 43 (1887).

In Table XLVII are given the results obtained by Cameron and Brown^a with solutions of ammonium nitrate.

TABLE XLVII.—*Solubility of calcium sulphate in solutions of ammonium nitrate at 25° C.*

Quantity NH ₄ NO ₃ per liter.	Quantity CaSO ₄ per liter.	Quantity NH ₄ NO ₃ per liter.	Quantity CaSO ₄ per liter.	Quantity NH ₄ NO ₃ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
10	3.18	200	9.85	1,000	11.81
25	3.93	300	10.80	1,200	11.10
55	5.80	400	11.40	1,400	10.02
100	7.65	450	12.02	Satu- rated.	7.55
150	8.88	750	12.20		

It will be observed that the solubility of calcium sulphate in ammonium nitrate solutions increases at first with increasing concentration of the more soluble salt, the maximum solubility being approximately 12.2 grams in a solution containing 750 grams of ammonium nitrate per liter. From this point, with increasing concentration of ammonium nitrate, the solubility of calcium sulphate decreases until both salts exist as solid phases, in which case the amount dissolved is 7.55 grams calcium sulphate per liter.

Potassium nitrate.

The solubility of gypsum, according to Vogel,^b is less in potassium nitrate solutions than in pure water. The results of Fassbender^c give the solubility of gypsum in saturated solutions of potassium nitrate at two temperatures. At 15.5° there is one part gypsum in 82 c. c. saturated KNO₃ solution, and at 20° there is one part gypsum in 69 c. c. of the saturated solution. Droeze^d confirms both these results and adds one more. At 13.5° there is one part gypsum in 94 c. c. saturated solution of KNO₃. Seidell and Smith^e have determined the solubility in different potassium nitrate solutions at 25°. The results are given in the following table:

TABLE XLVIII.—*Solubility of calcium sulphate in solutions of potassium nitrate at 25° C.*

Weight of 1,000 c. c. of solution.	Quantity KNO ₃ per liter.	Quantity CaSO ₄ per liter.	Weight of 1,000 c. c. of solution.	Quantity KNO ₃ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
998.1	0.0	2.084	1,092.4	150.0	7.907
1,008.1	12.5	3.284	1,122.4	200.0	8.688
1,015.4	25.0	4.080			f 6.278
1,032.1	50.0	5.255	1,153.9	260.0	g 12.112
1,062.5	100.0	6.855			

^a Jour. Phys. Chem., 9, 210 (1905).

^b Repert. Phar. (3), 5, 342 (1850).

^c Ber., 9, 1358 (1876).

^d Ber., 10, 330 (1877).

^e Jour. Phys. Chem., 8, 493 (1904).

^f Calculated from SO₄ determination.

^g Calculated from Ca determination.

Sodium nitrate.

The solubility of gypsum in sodium nitrate solutions as determined by Droeze ^a is as follows: 92 c. c. of a sodium nitrate solution saturated at 8.5° will dissolve 1 gram gypsum.

A more complete study has been made by Seidell and Smith, ^b whose results are given in Table XLIX.

TABLE XLIX.—*Solubility of calcium sulphate in solutions of sodium nitrate at 25° C.*

Weight of 1,000 c. c. of solution.	Quantity NaNO ₃ per liter.	Quantity CaSO ₄ per liter.	Weight of 1,000 c. c. of solution.	Quantity NaNO ₃ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
998.1	0	2.084	1,133.6	200	8.790
1,016.3	25	4.252	1,191.6	300	9.282
1,034.0	50	5.500	1,363.9	600	7.886
1,068.4	100	7.100	1,390.4	655	7.238

From this table it will be observed that the solubility of gypsum passes through a maximum where 300 grams of sodium nitrate are dissolved in a liter. Cameron and Brown ^c have determined the concentration of the solution in equilibrium with both salts at 25°. This solution contains 668.4 grams NaNO₃ per liter and 7.16 grams CaSO₄ per liter.

Magnesium nitrate.

The solubility of gypsum in magnesium nitrate solutions has been determined mainly by Seidell and Smith, ^d and the results of their work are tabulated in Table L.

TABLE L.—*Solubility of calcium sulphate in solutions of magnesium nitrate at 25° C.*

Weight of 1,000 c. c. of solution.	Quantity Mg(NO ₃) ₂ per liter.	Quantity CaSO ₄ per liter.	Weight of 1,000 c. c. of solution.	Quantity Mg(NO ₃) ₂ per liter.	Quantity CaSO ₄ per liter.
<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>	<i>Grams.</i>
998.1	0	2.084	1,149.8	200	13.340
1,020.5	25	5.772	1,219.0	300	12.000
1,039.8	50	7.884	1,282.1	400	14.683
1,078.6	100	9.920	1,355.3	514	15.040

The solution saturated with both salts at 25° has been found by Cameron and Brown ^c to contain 615.1 grams magnesium nitrate per liter and 15.26 grams CaSO₄ per liter.

Monochloroacetic acid and formic acid.

Two determinations have been made by Banthisch ^e on the effect of monochloroacetic acid on the solubility of gypsum. Solutions containing 46.87 and 93.74 grams monochloroacetic acid per liter dissolve 2.147 and 2.472 grams, respectively, of calcium sulphate per liter at 25° C.

^a Ber., 10, 330 (1877).^d Jour. Phys. Chem., 8, 493 (1904).^b Jour. Phys. Chem., 8, 493 (1904). ^e Jour. prakt. Chem., 137, 52 (1884).^c Jour. Phys. Chem., 9, 210 (1905).

This author has also found that a solution of formic acid containing 45.66 grams of acid per liter would dissolve 2.37 grams CaSO_4 per liter.

Phosphoric acid.

The solubility of gypsum in phosphoric acid solutions at 25° has been investigated recently in this laboratory by W. C. Taber. Solutions of phosphoric acid, to which solid gypsum have been added, have been analyzed for phosphoric acid, for lime, and for sulphuric acid. Equivalent amounts of lime and sulphuric acid have been found, indicating that there is no reaction between phosphoric acid and gypsum to produce a phosphate of calcium. The results of these experiments are as follows:

TABLE LI.—*Solubility of gypsum in phosphoric acid solutions at 25°C .*

Grams P_2O_5 per liter.	Grams CaSO_4 per liter.	Density of solu- tions 25°	Grams P_2O_5 per liter.	Grams CaSO_4 per liter.	Density of solu- tions 25°
0.0	2.126		145.1	7.920	1.106
5	3.143	1.002	205	8.383	1.145
10.5	3.734	1.007	311.5	7.965	1.221
21.4	4.456	1.016	395.8	6.848	1.280
46.3	5.760	1.035	494.6	5.572	1.344
105.3	7.318	1.075			

The table indicates that increasing amounts of phosphoric acid increase the solubility of gypsum at first, and above about 200 grams phosphoric anhydride per liter the solubility decreases. This is similar to the other electrolytes which have not an ion in common with gypsum.

Tartrate solutions.

Magnanini's experiments^a show that the solubility of gypsum is about 4.5 per cent greater in N/200 aqueous solution of cream of tartar at 20°C . than in water. If this solution of cream of tartar contains also 5 per cent of tartaric acid the solubility exceeds that in pure water by about 15 per cent. In 10 per cent aqueous alcohol the solubility of gypsum is only about 40 per cent of that in water and this solubility is still further depressed by the addition of cream of tartar to N/400. If, however, tartaric acid be now added to 5 per cent and the solution saturated at 20° with carbon dioxide the solubility is increased.

Sodium thiosulphate.

The solubility of gypsum in sodium thiosulphate solutions has been found by Diehl^b and Fuld^c to be much greater than in water, and the former attributes this increased solubility to the formation of a double thiosulphate of calcium and sodium.

^a Gazz. chim. ital. **31** ii, 542 (1901).

^c Jour. Chem. Soc., **16**, 28 (1863).

^b Jour. prakt. Chem., **79**, 430 (1860).

General remarks on the solubility of calcium sulphate in solutions of electrolytes which yield no common ion.

At very low concentrations, assuming that the salts are completely dissociated, the solubility of gypsum in the solution is influenced by the ions into which the salt is dissociated. The effect of compounds in solution with no common ion is to increase the solubility of gypsum, at least at the lower concentrations. This increase in solubility has been qualitatively found by Terreil^a in the case of ammonium salts. In the case of a very dilute solution of sodium chloride, for example, the increase in concentration may be ascribed to the combined effects of the two ions. Now, let us consider also a solution of potassium

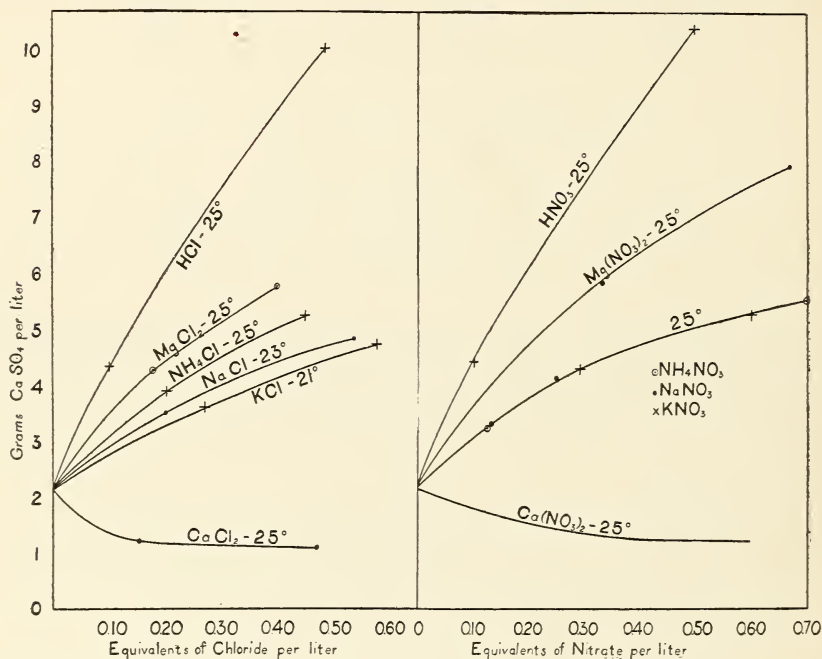


FIG. 9.—Solubility of calcium sulphate in chloride and nitrate solutions.

chloride of the same molecular concentration at the same temperature. The concentration of the chlorine ions is the same in the two solutions, which, barring slight differences in density, differ only in one respect, namely, the nature of the positive ion. The difference in the solubility of gypsum in the two solutions must be attributed to the different effects of the two positive ions. Taking dilute solutions of chlorides of equal content of chlorine, i. e., equivalent weights, we may compare the effect of the various positive ions. The solubility of gypsum has been plotted in the foregoing figure (fig. 9), the ordinates being the number of equivalents of the chloride in the solution. The curves are

^a Bul. Soc. Chim. (2), 9, 441 (1868).

for 25° in all cases for which the data was available, but where such was not available temperatures very close to 25° were taken; in the case of sodium chloride 23° and in the case of potassium chloride 21° . It is probable that if the result had been available at 25° the curves would have occupied a slightly higher position in the diagram. A similar figure has been drawn for the nitrates of hydrogen, magnesium, ammonium, sodium, and potassium. The position which these curves occupy relatively to one another is very interesting. The acids in both cases lie far above any of the salts, then the magnesium salts, and then the ammonium, sodium, and potassium, all together in the case of the nitrates, but separate in the case of the chlorides. This is probably due to the differences in temperature. From this it would appear that the solvent action of the positive ions investigated is greatest in the case of the hydrogen ion, somewhat less in the case of the magnesium ion, and least in the case of the sodium, potassium, and ammonium ions, which are of about the same power.

Comparing the chloride and nitrate of each metal, it will be seen that the nitrate possesses a slightly greater solvent action on gypsum than does the chloride.

Just as any of the physical properties of a dilute solution of a salt is the sum of the physical properties of the ions, the solvent action of these ions on a salt of comparatively low solubility is an additive property depending on the water and the two ions. In this way, if the data were determined with a high degree of accuracy, the difference between the solvent powers of every pair of cations might be accurately found, also the difference between the solvent power of every pair of anions. Thus, knowing the solvent action of NaCl, KCl, and NaNO_3 , the solvent action of KNO_3 might be computed.

In the case of the sulphates, the course of the curve, which falls with increase of the amount of the sulphate, has not been determined at low enough concentration to allow of any generalization.

In all the cases of the nitrates and the chlorides the course of the curve rises with addition of the other salt and passes through a maximum. This is what might be expected, for the concentrations of the calcium ion and of the sulphion are constantly increasing.

THE SOLUBILITY OF CALCIUM SULPHATE IN SOLUTIONS OF NONELECTROLYTES.

Alcohol.

The experiments of Magnanini^a show that gypsum is made less soluble in a 10 per cent alcohol solution than in water.

Sugar.

In an early paper on the solubility of gypsum in sugar solutions Sostmann^b has pointed out that a 67 per cent of sugar will dissolve

^aGazz. chim. ital., **31** ii, 542 (1901).

^bZeit. Rübenzuckerindustrie, **16**, 517 (1866)

0.163 per cent CaSO_4 , or, in other words, there is present 0.494 gram of CaSO_4 to 100 grams of water. Gypsum is more soluble in water containing sugar than in an equivalent amount of water. This result does not agree well with the results of Stolle,^a whose results are given in Table LII.

TABLE LII.—*Solubility of calcium sulphate in sugar solutions at different temperatures.*

Per cent sugar.	Quantity of CaSO_4 in 100 grams sugar solution.					
	At 30° C.	At 40° C.	At 50° C.	At 60° C.	At 70° C.	At 80° C.
	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>	<i>Gram.</i>
0	-----	0.2162	0.1733	0.1733	0.1655	0.1710
10	0.2045	.1733	.1733	.1576	.1576	.1613
20	.1811	.1655	.1421	.1382	.1421	.1263
27	.1557	.1440	.1363	.1285	.1285	.0972
35	.1265	.1051	.1089	.1109	.0915	-----
42	.1031	-----	.0777	.0817	.0856	.0729
49	-----	.0564	.0739	.0564	.0603	.0486
55	-----	.0886	.0505	.0486	.0369	.0330

This table shows that with increasing concentration the solubility of gypsum tends to decrease in sugar solution above 30° and also that the solubility in a given weight of solution decreases with increasing content of sugar.

Glycerine.

The solubility of gypsum in glycerine is given by Asselin^b as 0.95 part in 100 parts glycerine, at ordinary temperatures, the solubility increasing with the temperature.

CALCIUM SULPHATE IN SALT DEPOSITS AND IN ALKALI REGIONS.

The salts composing the accumulations known as "white alkali" are the same as those found in sea water. A great deal of work has been done on solutions containing these salts, especially for the purpose of elucidating the processes which have led to the deposition of salt deposits, and it is now possible to obtain a clear idea of the general features and characteristics of the system formed by calcium sulphate in contact with a solution of these several salts. This is the more readily done, since in a recent publication van 't Hoff^c has summarized a large portion of the work upon the deposition of salts from solutions containing the salts present in sea water. As the salt deposits have been laid down by the constant evaporation of sea water, a knowledge of the conditions under which each salt separates will indicate the conditions which obtained in nature during the deposition. The salts present in sea water and in "white alkali" are mainly the chloride and sulphates of sodium, potassium, and magnesium. Calcium salt

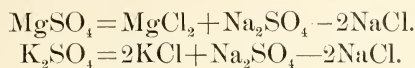
^a Zeit. Rübenzuckerindustrie, **37**, 321 (1900).

^b Compt. rend., **76**, 884 (1873).

^c Zur Bildung der ozeanischen Salzablagerungen, Braunschweig, 1905.

are present, for calcium appears in deep salt deposits as anhydrite and in surface deposits as gypsum. The influence of the presence of calcium will be discussed after a consideration of the other salts.

Let us first consider the number of components in a solution containing the chlorides and sulphates of sodium, potassium, and magnesium. Apparently there are seven—water, NaCl , Na_2SO_4 , KCl , K_2SO_4 , MgCl_2 , and MgSO_4 . But there are two possible relations existing among these, so that the number can be considered as reduced to five. The relations are that magnesium sulphate and potassium sulphate may be expressed in terms of the other salts, thus,



The phase rule requires that under no circumstance can the number of phases exceed the number of components by more than two. The maximum number of phases that can exist under equilibrium conditions is, therefore, seven. The coexistence of seven phases is possible, however, only at definite temperatures, and for any temperature in general the maximum number of phases that can exist is six.

There is present in sea water and generally in "white alkali" a predominating amount of sodium chloride, and in salt mines there is found sodium chloride in all layers, which has crystallized out with one or more other salts. Van 't Hoff has imposed the condition in all his experiments that the solution shall be saturated with sodium chloride, or in other words that sodium chloride shall be always present as a solid. In his experiments the solution and the vapor are two other phases, leaving a maximum possibility of three other solid phases, unless the temperature happens to be that of a univariant system, in which case there will be four other solid phases.

In the solution there may be any or all of six salts, one of them always being sodium chloride. As was stated above, there are two relations between these six quantities, making four the least number of variables in which the concentration may be expressed. In stating the results of the analyses of the solutions, van 't Hoff has adopted two arbitrary conventions—first, as the amount of potassium never exceeds the amount of chloride, the potassium shall always be expressed as potassium chloride; and second, all the remaining chlorine is considered as sodium chloride (NaCl), unless chlorine be in excess over sodium, in which case all the sodium is expressed as sodium chloride. Thus the greatest amount of sodium chloride possible is considered to be present. The residue is expressed as sodium sulphate (Na_2SO_4) and magnesium sulphate (MgSO_4), or as magnesium chloride (MgCl_2) and magnesium sulphate (MgSO_4), as the case may be.

All the possible solutions as given by van 't Hoff are expressed in terms of NaCl , KCl , MgSO_4 , and Na_2SO_4 , or in terms of NaCl , KCl ,

MgSO_4 , MgCl_2 , and it is necessary, therefore, to use two diagrams or sets of axes in order to represent all the conditions. Two diagrams have been joined, as indicated in figure 10. The solutions represented by the one set of variables are plotted with MgCl_2 concentrations for abscissas and $(\text{K}_2\text{Cl}_2 - \text{MgSO}_4)$ concentrations for ordinates, and the solutions represented by the other set of variables are plotted with Na_2SO_4 concentrations as abscissas and $(\text{K}_2\text{Cl}_2 - \text{MgSO}_4)$ concentrations for ordinates.

The procedure adopted by van 't Hoff and his coworkers has been to determine what solid phases could appear at 25°C. , and then to determine the range of concentrations of the solution within which each one exists. The phase rule prescribes the maximum number of phases which may exist if there are a given number of components present, the conditions being known as invariant. These invariant points

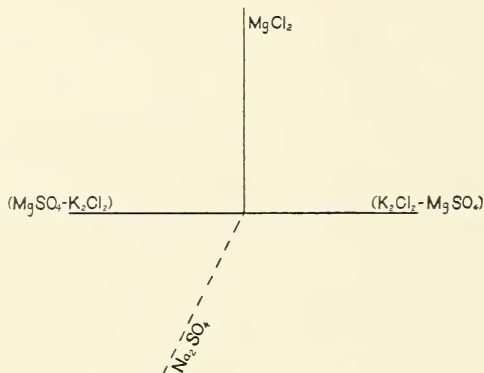


FIG. 10.—Coordinates used in figure 11.

have been found—i. e., the compositions of the “constant” solutions have been determined. In the following table the composition of these solutions have been given. For instance, at the point **O**, in figure 11, the only salt present is sodium chloride, and the invariant point at 25° is the solution saturated with this salt; at the point **A** the salts are magnesium chloride and sodium chloride, and the composition of the solution saturated with both these salts is given in the table. At any other point on the diagram, **P** for instance, there are present as solids kainite, leonite, and sylvine, and the composition of this solution in equilibrium with these three solids has been given in the table. The significance of the column headed by “ CaSO_4 ” will be discussed later.

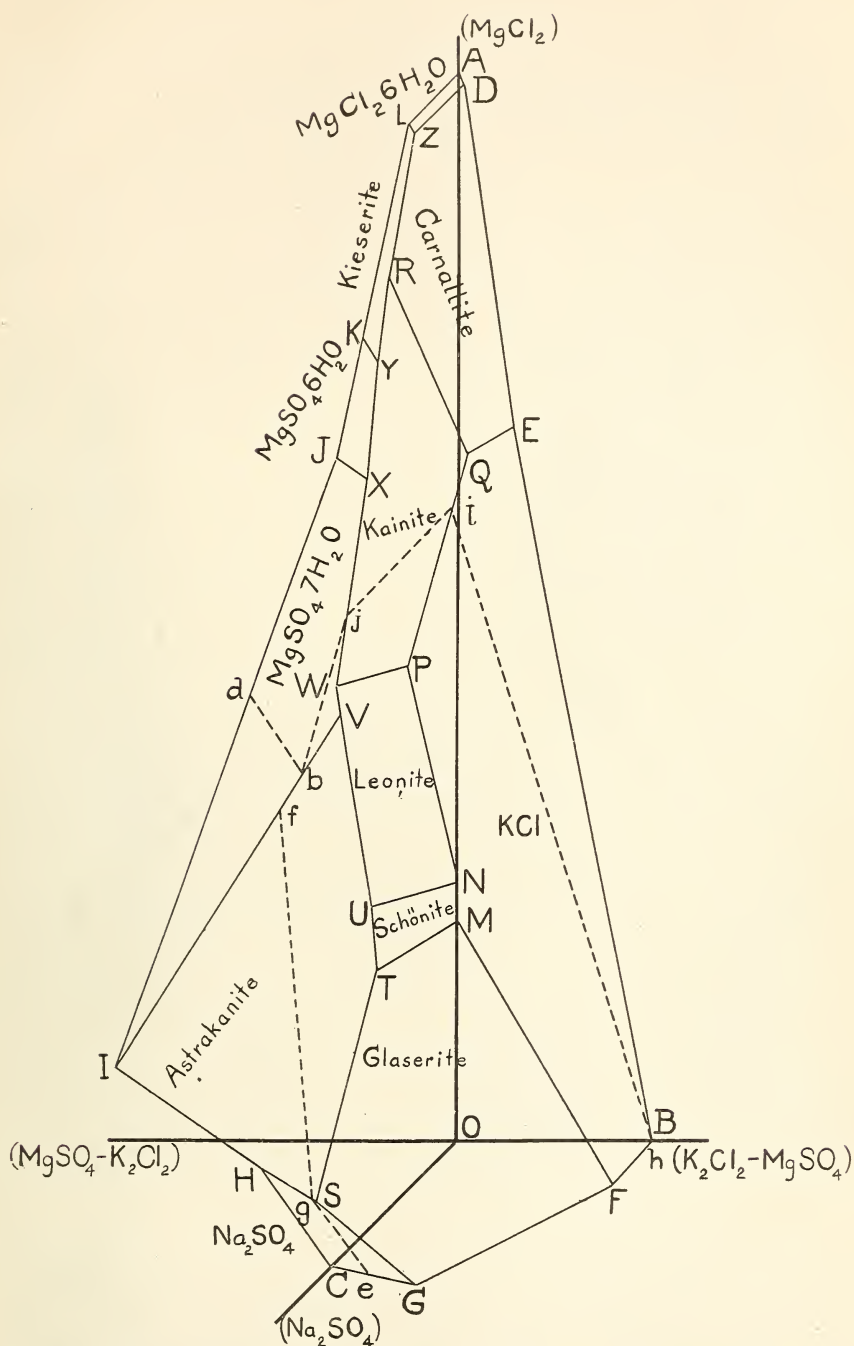


FIG. 11.—Diagram showing the mutual solubilities of the salts present in the sea-water deposits.

TABLE LIH.—Composition of solutions at "constant" or invariant points on the diagram (fig. 11) at 25° C.

Corresponding points on diagram.	Solids with which "constant" or invariant solutions are saturated, sodium chloride always being present.	Quantity of several salts in 1,000 mols. of H ₂ O solution.						Vapor pressure of the solution.
		Na ₂ Cl ₂ .	K ₂ Cl ₂ .	MgCl ₂ .	MgSO ₄ .	Na ₂ SO ₄ .	CaSO ₄ .	
		Mols.	Mols.	Mols.	Mols.	Mols.	Mols.	Mm. Hg.
O		55.5					0.86	17.7
A	MgCl ₂ .6H ₂ O	1		106			.39	7.6
B	KCl	44.5	19.5				.94	16.8
C	Na ₂ SO ₄	51				12.5	.05	17.5
D	MgCl ₂ .6H ₂ O, carnallite	1	.5	105			.38	7.5
E	KCl, carnallite	2	5.5	70.5			.26	12.7
F	KCl, glaserite	44	20			4.5	.03	16.8
G	Na ₂ SO ₄ , glaserite	44	10.5			14.5	.02	17
H	Na ₂ SO ₄ , astrakanite	46			16.5	3	.04	17.1
I	MgSO ₄ .7H ₂ O, astrakanite	26		7	34		.0	15.1
J	MgSO ₄ .7H ₂ O, MgSO ₄ .6H ₂ O	4		67.5	12		.19	12.2
K	MgSO ₄ .6H ₂ O, kieserite	2.5		79	9.5		.12	10.8
L	Kieserite, MgCl ₂ .6H ₂ O	1		101	5		.25	7.5
M	KCl, glaserite, schönite	23	14	21.5			.08	15.9
N	KCl, schönite, leonite	19.5	14.5	25.5	14.5		.09	15.7
P	KCl, leonite, kainite	9.5	9.5	47	14.5		.13	13.4
Q	KCl, kainite, carnallite	2.5	6	68	5		.24	12.4
R	Carnallite, kainite, kieserite	1	1	85.5	8		.13	9.5
S	Na ₂ SO ₄ , glaserite, astrakanite	42	8		16	6	.06	16.6
T	Glaserite, astrakanite, schönite	27.5	10.5	16.5	18.5		.08	16.1
U	Leonite, astrakanite, schönite	22	10.5	25	19		.08	15.7
V	Leonite, astrakanite, MgSO ₄ .7H ₂ O	10.5	7.5	42	29		.1	14.5
W	Leonite, kainite, MgSO ₄ .7H ₂ O	9	7.5	45	18.5		.09	13.4
X	MgSO ₄ .7H ₂ O, kainite, MgSO ₄ .6H ₂ O	3.5	4	65.5	15		.2	12.2
Y	MgSO ₄ .6H ₂ O, kainite, kieserite	1.5	2	77	10		.21	10.8
Z	Carnallite, MgCl ₂ .6H ₂ O, kieserite	1	.5	100	5		.15	7.4

The possible minerals which may appear by allowing a solution of the sulphates and chlorides of magnesium, potassium, and sodium to crystallize at 25° are given in the following table. The table gives also the composition of these minerals and the field in diagram (fig. 11) within which they exist.

TABLE LIV.—Chemical composition and field within which each solid phase exists.

Mineralogical name.	Solid phase.	Field.
Bischofite	MgCl ₂ .6H ₂ O	A L Z D.
Sylvine	KCl	B F M N P Q E.
Thenardite	Na ₂ SO ₄	C G S H.
Carnallite	MgCl ₂ .KCl.6H ₂ O	D Z R Q E.
Glaserite	2K ₂ SO ₄ .Na ₂ SO ₄	F R T S G.
Astrakanite	Na ₂ SO ₄ .MgSO ₄ .4H ₂ O	S H I V U T.
Reichardtite	MgSO ₄ .7H ₂ O	J X W Y L.
	MgSO ₄ .6H ₂ O	J X Y K.
Kieserite	MgSO ₄ .H ₂ O	K Y R Z L.
Schönite	MgSO ₄ .K ₂ SO ₄ .6H ₂ O	T U V M.
Leonite	MgSO ₄ (K, Na) ₂ SO ₄ .4H ₂ O	N U V W P.
Kainite	MgSO ₄ .KCl.3H ₂ O	P W X Y R Q.

The vapor pressures of the solutions at the various points in the figure have been determined at 25°, and in this way the path along which the concentration of the solution during evaporation will move has been determined. During evaporation at constant temperatures the end-point in the evaporation will be that solution which has the

lowest vapor pressure. The paths along which the solution moves have been determined by van 't Hoff and his coworkers. It has been found that the end-point is **Z**, at which carnallite, kieserite, and bischofite crystallize out together. It should be noticed that in the evaporation of sea water the first solid which separates is gypsum, the solution being so dilute at first that gypsum and not anhydrite is the stable phase, then sodium chloride appears in quantity. The first mineral composed of the other salts is kainite, the solution being represented in the diagram by a point in the kainite field near the line **R Y**. At this point the stable phase containing calcium is anhydrite, and in all subsequent crystallization from these concentrated solutions anhydrite is to be expected. By further evaporation a point on the line **R Y** is reached, at which both kainite and kieserite separate until **R** is reached. Then kieserite and carnallite separate until the point **Z** is reached, and finally the three phases, kieserite, carnallite, and bischofite. The same phases, sodium chloride, kieserite, carnallite, and bischofite are also the final products when sea water is evaporated at 83°. Several other salt layers are actually formed, polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$) and langbeinite ($2MgSO_4 \cdot K_2SO_4$). The alternate layers of anhydrite and common salt are probably due to the varying temperature at which the salt layers have been deposited. For instance, anhydrite is less soluble, while sodium chloride is somewhat more soluble, in hot water than in cold. Thus, during a warm season anhydrite would crystallize out, and when the solution became colder sodium chloride would crystallize out. At the surface anhydrite would gradually be transformed into gypsum by taking up water from the atmosphere.

The introduction of one more component to the system will in general alter the whole situation. But the introduction of the salt calcium sulphate ($CaSO_4$) to the solution has very little influence on the position of any point in the diagram, because the amount of calcium sulphate in solution is very small, and this very small amount does not alter appreciably the solubility of the other salts. The amount of calcium sulphate in solution and corresponding to each of the points in the diagram is given in Table LV. Therefore practically the same state of affairs exists as before the addition of the calcium sulphate, except for the fact that one more phase may appear, a phase containing calcium sulphate. Consequently another set of fields is superimposed on the double diagram representing the solid phases which contain calcium sulphate. These fields are three in number and are marked out by broken lines—the field **L d b j i h B A**, in which anhydrite ($CaSO_4$) is the solid phase, the field **d b g e C I**, in which glauberite ($CaSO_4 \cdot Na_2SO_4$) is the solid phase, and the field **e g f j i h G**, in which syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$) is the solid phase. It will be observed that anhydrite is the stable solid phase in the part

of the field where the evaporation of sea water is represented, and hence anhydrite is practically the only form in which calcium sulphate appears in the deep salt deposits.

The concentration of the solutions at the various points along these new boundary lines are given in the following table:

TABLE LV.—Composition of solutions containing calcium sulphate at "constant" or invariant points on the diagram at 25° C.

Corresponding points on diagram (fig. 11).	Solids with which "constant" or invariant solutions are saturated, sodium chloride always being present.	Quantity of salts in 1,000 mols. of H ₂ O.						Vapor pressure of the solution.
		Na ₂ Cl ₂ .	K ₂ Cl ₂ .	MgCl ₂ .	MgSO ₄ .	Na ₂ SO ₄ .	CaSO ₄ .	
b	Anhydrite, glauberite, syngenite, MgSO ₄ .7H ₂ O, astrakanite	Mols. 13.5	Mols. 5	Mols. 36	Mols. 20	Mols.	Mols. .08	Mm. Hg. 14.4
d	Glauberite, anhydrite, MgSO ₄ .7H ₂ O						.1	14.4
e	Glauberite, syngenite, Na ₂ SO ₄ .	47	5.5			14	.03	17.3
f	Glauberite, syngenite, astrakanite, MgSO ₄ .7H ₂ O	14.5	5.5	32.5	23		.07	14.4
g	Glauberite, syngenite, astrakanite, Na ₂ SO ₄ .	41.5	8.5		16.5	5.5	.06	16.6
h	Syngenite, anhydrite, KCl	46	19.5				.85	16.8
i	Syngenite, anhydrite, kainite, KCl	4.5	7	62.5	7.5		.21	12.7
j	Syngenite, anhydrite, kainite, MgSO ₄ .7H ₂ O	7	6.5	52	17.5		.13	12.9

More recently^a the existence of two other fields has been proved, but these are very small and are not represented in the diagram. The boundary for the phase polyhalite (K₂SO₄.MgSO₄.2CaSO₄.H₂O) has been found to cut a small portion from the field for syngenite. It passes through **b** around the points **W** and **V** and cuts the line **f g** near **f**. Another small field is a long, narrow strip bounded by **i**, **h**, and points in **i j** and **h f** near **i** and **h**, respectively. In this field the stable phase is potassium pentacalcium sulphate (K₂SO₄.5CaSO₄.H₂O).

Gypsum (CaSO₄.2H₂O) is the solid phase in a very small field just at the point **h**, cutting off a very small portion from the field for anhydrite^b, and a field for krugite (4CaSO₄.K₂SO₄.MgSO₄.2H₂O) cuts off a very thin portion of the anhydrite field just at the point **j**.

If instead of the crystallization of a brine we follow the course of the washing out of a mixture of salts by water, the composition of the solution which results will depend only on the solid phases which are present and not on their relative amounts. When any one of the solid phases becomes completely washed out, the composition of the solution will change. This washing-out process has been followed by this Bureau and analyses of the drainage water of the Swan tract near Salt Lake City have been tabulated at intervals extending over three years. The accumulation of alkali at the surface of soils is due mainly to the

^a Van 't Hoff and Farup, Sitzungsber. Akad. Wiss. Berlin (1903), 1,000; van 't Hoff and Voerman, *ibid.* (1904), 984; van 't Hoff, *ibid.* (1904), 935.

^b Van 't Hoff, *Zeit. anorg. Chem.*, **47**, 244 (1905).

evaporation of seepage waters from lower levels. These seepage waters will in all probability have a constant composition as the water has become saturated with respect to all the constituents of the salts in the lower depths. In the converse process of washing out the solution should have a constant composition throughout. This has actually been found to be the case in the Swan tract, where the percentage of alkali salts in the soil has decreased as a result of flooding from more than 2.7 per cent to less than 0.3 per cent. The composition of the drainage water has, however, remained approximately constant throughout the whole period.

Of course the composition will depend upon the temperature and therefore on the season, and also, as calcium sulphate goes into solution at a very slow rate indeed, the composition of the drainage water will depend on the time of contact of the irrigation water with the soil. These results have been given on page 10 of this bulletin.

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